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A MIGRATION METHOD FOR THE DETERMINATION OF REPLACEABLE BASES IN SOILS[1]

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In connection with studies of calcareous hardpans, it is often desirable to determine the ratio of the replaceable bases in the different horizons of the soil profiles under investigation. The common occurrence of calcium and magnesium carbonates in these soils makes it necessary to use some method not seriously affected by such salts but capable of strongly differentiating those soil conditions that are affecting crop production. In the course of such studies at this station, two commonly utilized methods and one new one have been investigated. The results obtained with the new method warrant calling especial attention to it. Indications are that this means of study may bring out new conceptions, especially with regard to the ratio of the replaceable bases to one another.

REVIEW OF LITERATURE

Several methods for determining the replaceable bases in soils have been proposed. Kelley and Brown (5) and Chapman and Kelley (4) recommend the use of normal solutions of ammonium chloride or ammonium acetate, which are used to leach the soil successively. The use of such solutions requires the leaching of a small soil sample with relatively large amounts of solution, ratios of 1 part of soil to 40 parts of solution being quite general. In these methods the solubility of certain minerals is a disturbing factor for which corrections are difficult to make. The most common difficulty is the relatively great solubility of calcium and magnesium carbonates in solutions of ammonium salts. In certain cases, also, organic matter is dissolved, and the absorbing complex may be thereby altered in composition as the leaching proceeds.

Burgess and Breazeale (3) and Magistad and Burgess (10) have suggested methods for the determination of replaceable bases in calcareous soils. Burgess and Breazeale suggested the use of 0.1 *N* $BaCl_2$ solution for leaching the soil, and showed that there was negligible solubility of the alkaline earth carbonates in this solution. It seems possible, however, that the weaker solution would not react quite so strongly with the absorbing complexes, although Magistad and Burgess claim to have found that concentration made but little difference. Since we are dealing with a series of simultaneous equilibrium reactions, as is evident from the apparent need for successive leachings to complete them, it seems unusual if concentration plays no part. The effect of the concentration of one salt in solution upon the reaction of other substances in mixtures is usually important, and in replacement reactions in soils several salts are generally present at once. These authors suggested the use of alcoholic salt solutions for leaching. The dehydrating effect of alcohol on the colloidal complexes,

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which would undoubtedly alter their reactivity, makes such procedure appear too artificial to indicate what the soil behavior would normally be in an aqueous medium. Ultimate use of replacement data would normally be made in a soil-water system.

The use of electrodialysis (2) to determine the replaceable bases in soils would be extremely simple and satisfactory if there was a certainty that the character of the complex was not changed during the determination. The reaction changes so strongly that the pH value of the electrodialyzed soil often reaches a value of 2.5, and appreciable quantities of aluminum appear in solution. This aluminum may be derived from the breakdown of the colloidal complex itself, and the solubilities of many other components is undoubtedly increased. Such a drastic change in soil reaction must considerably upset the normal equilibrium under which the results of the determination are to be applied.

Two main difficulties in connection with present methods of determining replaceable-bases must be overcome. One involves the elimination of the excessive solubility effects in leaching methods, and the second involves the elimination of artificial and drastic changes in the complex itself during the extraction.

In 1923 Kendall and Crittenden (6), and in 1924 Kendall and White (7) made separations of the isotopes of chlorine by means of an ionic migration method. The following year certain rare earths were separated by the same procedure by Kendall and Clarke (8). The method is essentially one in which the substances to be separated are dissolved and imbedded in a plug of agar in a cylindrical glass tube of suitable dimensions. Other electrolytes are mixed with agar and placed in contact with the agar plug containing the substances to be examined. It is necessary to have a faster moving ion in the agar ahead of the plug to be examined, and a slower moving one following, in order to preserve the sharp boundaries of the original material. One colored ion may be employed to indicate the course of the migration. Thus, if calcium and magnesium were in the original plug of agar, it would be necessary to use some cation with a higher mobility between them and the cathode toward which they will migrate. Following them should be a slower, colored cation. The concentrations best adapted for leading and following ions are suggested by the relation $\frac{C}{T} = \frac{C'}{T'}$, where C and C' = equivalent concentrations and T and T' = transference numbers of the cations.

An attempt has been made to use this method for the extraction of replaceable bases in soil. It was found that the ammonium ion is a relatively fast moving cation exceeding all of those in the soil except H ion. It can thus be used for replacement, and lends itself readily for use as the leading ion during migration. Cobalt ions, colored red, are slower moving than the soil bases and make excellent following ions.

The absolute ionic velocities of the bases we are interested in, at a temperature of 18°C., and at unit potential gradient, are as follows:

	cm. per second
Hydrogen	0.003242
Ammonium	0.000668
Potassium	0.000665
Calcium	0.000534
Magnesium	0.000471
Sodium	0.000456
Cobalt	0.000420*

* Determined in 2 per cent agar at a potential gradient of about 2 volts/cm. Value only approximate.

EXPERIMENTAL METHODS

Methods of replacement

Tenth-normal barium chloride method. According to the directions of Burgess and Breazeale, 100 gm. of soil is placed in a glass percolating tube and

leached with 700 cc. or more of 0.1 *N* $BaCl_2$ solution until free from replaceable calcium. The percolate is then filtered, if necessary, and made up to a standard volume, from which aliquot samples are taken for analysis. The details of the special methods suggested to eliminate the excessive quantities of barium salts need not be mentioned. In this work, the standard methods suggested by the authors were employed.

Normal ammonium acetate method. Ten-gram samples of oven-dry soil are weighed into 400-cc. Erlenmeyer flasks, and 250 cc. of normal ammonium acetate solution is added to each. The flasks are kept at a temperature of 70°C. on top of a steam bath for about 15 hours and then their contents are poured on a filter and washed three times with 50-cc. portions of hot extracting solution, finally making the volume of leachate exactly 400 cc. Aliquots of this solution are then taken for analysis. It was found in a separate experiment that 400 cc. of a saturated solution of $CaCO_3$ in normal ammonium acetate solution contained 297.6 mgm. of Ca, which was used as a correction figure whenever the soil sample contained carbonates.

Migration method. Ten grams of oven-dry soil is weighed out, in a glass weighing scoop, and 10 cc. of hot normal ammonium acetate added slowly, the entire soil mass being carefully saturated. The mixture is allowed to stand about 1 hour. Meanwhile, a glass tube about 2.5 cm. in diameter and 45 cm. long is stoppered at one end, and melted 2 per cent agar in normal ammonium acetate is poured in. When solid, the column of agar is trimmed to a length of 25 cm. A wash bottle containing hot 2 per cent agar in normal ammonium acetate is used to wash the soil from the glass scoop into the cylinder. The length of the agar-soil plug should not be greater than 8 cm. When this is cooled, a hot 2 per cent agar solution, made up with 0.5 *N* cobalt acetate, is used to fill the cylinder. When cool, the end of the cobalt agar may be cut off to expose a clear bubble-free surface. The tube now consists of 25 cm. of ammonium acetate agar on one end, 8 cm. or less of soil-ammonium acetate agar in the center, and 12 cm. of cobalt acetate agar on the other end.

Two sets of two rubber stoppers on short pieces of glass tubing of about 1.5 cm. diameter are placed top to top with the tubes extending only to the ends of the stoppers. These are inserted into the ends of the cylinder containing the agar and should support the agar column firmly at each end. On each end of the cylinder a suction flask is now attached. In the flask, at the cobalt agar end, is placed a 0.5 *N* solution of cobalt acetate, into which a platinum electrode is inserted through the suction tip of the flask. Into the other flask is placed a normal solution of copper acetate and a copper electrode is inserted through the suction tip. The two electrodes are connected with a direct current generator, so that the copper electrode becomes the negative electrode. This insures the migration of the cations into the end of the tube containing ammonium acetate agar. The whole set-up may be supported by ring stands and clamps. Figure 1 illustrates the essential points in the experimental arrangement.

A current of about 110 volts and 0.5–0.6 amperes is passed through the tube until cobalt ions appear at the other end of the soil-agar plug. This requires from 5–6 hours. At the end of this time all faster moving free ions are out of the soil. The electrode flasks are disconnected, and the ammonium acetate agar plug containing the cations which have been replaced in the soil and have migrated out of it, is cut into suitable lengths, placed in a 100-cc. quartz evaporating dish, and after a few drops of sulfuric acid have been added is evaporated to dryness in an oven at 105°C. Ignition at red heat in a muffle furnace leaves a white ash, which is dissolved in hot water and a few drops of hydrochloric acid, and the volume made up to 200 cc. or other convenient quantity. Aliquots of this solution can be taken for analysis of calcium, magnesium, sodium, and potassium.

Purified agar should be employed in this procedure, but even the best quality material contains appreciable amounts of the bases also present in the soil. A blank determination of base content, using a column of normal ammonium acetate agar of the same length and from the same tube that will be used in the

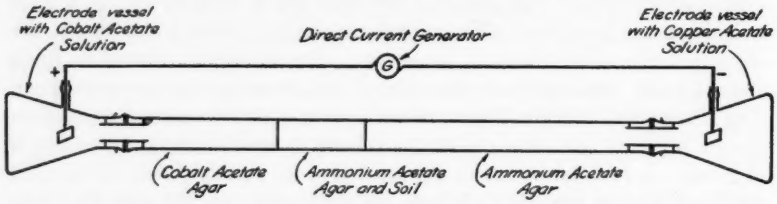

FIG. 1. EXPERIMENTAL ARRANGEMENT FOR EXTRACTING THE BASES FROM SOILS BY THE MIGRATION METHOD

soil studies, should be made. In the studies here reported it was found that the agar column contained 11.2 mgm. Ca, 6.12 mgm. Mg, 142 mgm. K, and 3.76 mgm. Na. These values are subtracted from the values obtained in the regular analysis after migration.

Methods of analysis

Calcium. The method outlined by Burgess and Breazeale was used to determine this element in extracts obtained by their method. In the other methods, official volumetric methods were used.

Magnesium. The method of Burgess and Breazeale was used for extracts made according to their method. In other studies, official gravimetric methods were employed.

Potassium. The sodium cobalti-nitrite method of Kramer (9) with certain modifications was used throughout these studies, titrations being made with 0.1 *N* potassium permanganate. The barium salts in the Burgess-Breazeale method were removed in accordance with directions given by them.

Sodium. The method of Barber and Kolthoff (1) utilizing the zinc uranyl acetate reagent was used, and the precipitate dried and weighed. A barium-

free solution was obtained in the same manner as used in the determination of potassium.

SOILS

Ten soils were selected for the preliminary comparison of methods. Four contain carbonates and are strongly alkaline; three are slightly alkaline or faintly acid; and two are strongly acid in reaction. In texture they vary from fine sandy loam to clay loam. One sample consists of calcareous hardpan material. Table 1 gives some of the more important characteristics of the samples.

TABLE 1

Characteristics of the soils used in this investigation

LOCATION OF SOIL	TEXTURE	COLLOIDAL CONTENT	pH VALUE	QUANTITY OF CARBONATES	OTHER CHARACTERISTICS
		per cent		*per cent*	
Prosser 1	Fine sandy loam	18	8.60	1.44	Arid—sage brush soil
Prosser 2	Fine sandy loam	19	8.57	0.75	Arid—sage brush soil
Prosser 3	Fine sandy loam	18	8.40	0.81	Arid—sage brush soil
Colton	Silt loam	31	7.25	....	Semi arid—prairie soil
LaCrosse	Silt loam	30	7.12	....	Semi arid—prairie sage
Washtucna	Fine sandy loam	20	7.65	....	Arid—sage brush soil
Woodland	Clay loam	32	4.70	....	Humid—residual forested
Albion	Silt loam	26	5.85	....	Semi arid—prairie soil
Walla Walla 1	Silt loam	22	6.10	....	Semi arid—prairie soil
Walla Walla 2	Hardpan	..	9.00	7.92	Sage—White alkali land

TABLE 2

Milliequivalents of replaceable bases per 100 gm. of soil as determined by the method of Burgess and Breazeale using 0.1 N $BaCl_2$ solution

SOIL	MILLIEQUIVALENTS PER 100 GM. OF SOIL				
	Calcium	Magnesium	Potassium	Sodium	Sum
Prosser 1	11.78	2.06	0.26	1.63	15.73
Prosser 2	11.92	1.78	0.18	1.76	15.64
Prosser 3	11.66	1.68	0.19	2.08	15.61
Colton	18.00	5.63	0.61	0.34	24.58
LaCrosse	11.25	3.80	0.99	0.39	16.43
Washtucna	10.00	2.90	1.10	0.42	14.42
Woodland	10.50	4.75	0.58	0.22	16.05
Albion	14.55	3.00	0.38	0.61	18.54
Walla Walla 1	11.95	2.33	0.75	0.27	15.30
Walla Walla 2	7.62	3.27	1.85	2.98	15.72

EXPERIMENTAL RESULTS

Tenth-normal barium chloride method

The results obtained when 100 gm. of soil is leached with successive 50-cc. portions of 0.1 *N* $BaCl_2$ until a volume of about 700 cc. is obtained are given in table 2. From 65–78 per cent of the sum of the bases analyzed consists of calcium, and this element with magnesium makes up the greater part of the total. The amount of replaceable sodium exceeds the magnesium in only one case, and is usually considerably smaller. The quantities of exchangeable potassium are small, varying from about 1 to 11 per cent of the total replaceable bases analyzed. The method indicates that the alkaline earth bases are dominant in all soils except the hardpan material. The Woodland sample is a strongly leached residual soil derived from basaltic rocks, and it would appear that the method does not differentiate this strongly enough to show its marked

TABLE 3

Milliequivalents of replaceable bases per 100 gm. of soil as determined by the method of Chapman and Kelley using normal ammonium acetate solution

SOIL	MILLIEQUIVALENTS PER 100 GM. OF SOIL				
	Calcium	Magnesium	Potassium	Sodium	Sum
Prosser 1	46.62	4.91	1.00	1.09	53.62
Prosser 2	35.12	5.55	1.27	1.10	43.04
Prosser 3	25.62	5.64	1.63	1.08	33.97
Colton	19.25	6.28	1.45	1.01	27.99
LaCrosse	12.50	4.27	1.81	0.88	19.46
Washtucna	12.75	4.01	2.57	0.93	20.25
Woodland	11.75	6.19	1.18	0.91	20.03
Albion	16.50	4.91	1.05	0.91	23.37
Walla Walla 1	15.75	5.17	1.09	0.76	21.07
Walla Walla 2	93.12	18.93	1.81	7.40	121.26

difference in character from the rest of the samples. The Colton sample is more severely leached than the LaCrosse sample and contains about the same amount of colloidal material; yet more alkaline earth bases are shown by this method in the Colton soil. The results do not quite provide a logical basis for the explanation of the behavior of these soils in the field, and this may be the result of a tendency to replace more completely the alkaline earth bases than the alkali bases. The work of Burgess and Breazeale shows that this 0.1 *N* $BaCl_2$ solution does not directly dissolve appreciable amounts of calcium, and yet proportionally large amounts of the totals replaced and analyzed are made up of calcium and magnesium.

Normal ammonium acetate method

The results obtained with the normal ammonium acetate method, when carried out in the manner already described, are shown in table 3. These data

show a much greater energy of replacement, as can be noted by observing the totals analyzed in this and the preceding table. But again the alkaline earth bases are shown to be dominant, and in some cases their importance is undoubtedly greatly exaggerated, on account of solubility effects which cannot be entirely corrected. Thus, from 58–86 per cent of the total bases found by analysis consist of calcium alone, and in many cases over 90 per cent of the total is alkaline earth bases. The part that sodium and potassium play in the field behavior of these soils is masked by the solubility of the calcium and magnesium, especially in the case of calcareous soils.

Migration method

Table 4 contains the data obtained with the migration method in which the replaceable bases are extracted after a single treatment with normal ammonium

TABLE 4

Milliequivalents of replaceable bases per 100 gm. of soil as determined by the migration method, using normal ammonium acetate as replacing solution

SOIL	MILLIEQUIVALENTS PER 100 GM. OF SOIL				
	Calcium	Magnesium	Potassium	Sodium	Sum
Prosser 1	13.44	4.82	1.70	5.79	25.75
Prosser 2	12.64	4.65	1.01	4.58	22.88
Prosser 3	11.44	3.66	0.81	4.49	20.40
Colton	12.94	8.95	1.36	2.46	25.71
LaCrosse	12.44	9.05	1.54	2.81	25.84
Washtucna	13.69	9.68	1.80	2.28	27.45
Woodland	7.44	3.65	1.35	3.16	15.60
Albion	12.77	8.65	1.78	3.14	26.34
Walla Walla 1	8.69	4.49	1.36	1.77	16.31
Walla Walla 2	13.44	7.77	2.49	10.88	34.58

acetate solution. There is a general agreement between the results of the Burgess and Breazeale method and this one, with respect to calcium, although sometimes larger and sometimes smaller amounts are obtained with the migration method. In all except one case, more magnesium is obtained by the migration method than by the 0.1 *N* $BaCl_2$ method. Generally the magnesium obtained by the normal ammonium acetate method and by the migration method are comparable, sometimes one and sometimes the other being greater. The most striking difference shown by the migration method is the relatively strong replacement of potassium and sodium, especially the latter. In every soil the replaceable sodium obtained through migration procedure exceeds that obtained by the leaching methods. This makes the results of this method especially valuable in the study of alkali soils and hardpan formation, because it shows the influence of the alkali bases and offers a suggestion for the field behavior of these soils, which is not brought out by other methods. Why the

leaching methods fail to extract as much sodium as the migration method can only be suggested, but some preferential solution process may inhibit the sodium release and stimulate the calcium and magnesium release. The migration method apparently indicates more clearly the true ratio of the various replaceable bases, for it is not involved by abnormal solubilities as a result of leaching and yet it is capable of obtaining from the soil complexes at least the same amounts of both calcium and magnesium as can be obtained by the other two methods. Moreover, it has been found that the pH values of the soils after the migration procedure are about the same as those obtained on the original samples.

Ratios of the replaceable bases

A clearer picture of the ratios of the replaceable bases to one another can be obtained by a study of the material presented in table 5. The ratio of alkali

TABLE 5

A comparison of the replaceable base ratios in the soils treated by the different methods indicated

SOIL	$\frac{Ca+Mg}{Na+K}$ RATIOS			$\frac{Ca}{Mg}$ RATIOS		
	0.1 N $BaCl_2$	N NH_4Ac	Migration	0.1 N $BaCl_2$	N NH_4Ac	Migration
Prosser 1	7.32	24.65	2.43	5.71	9.49	2.78
Prosser 2	7.06	17.16	3.09	6.69	6.32	2.71
Prosser 3	5.87	11.53	2.84	6.94	4.54	3.12
Colton	24.87	10.37	5.73	3.19	3.06	1.44
LaCrosse	10.90	6.23	4.94	2.96	3.11	1.37
Washtucna	8.48	4.78	5.72	3.44	3.17	1.41
Woodland	19.16	8.58	2.45	2.21	1.89	2.03
Albion	17.92	10.92	4.35	4.60	3.36	1.47
Walla Walla 1	14.00	10.38	4.21	5.12	3.04	1.93
Walla Walla 2	2.25	12.16	1.58	2.34	4.92	1.72

to alkaline earth bases in exchangeable form as determined by the different methods varies between wide limits. The average ratio, for instance, for all 10 soils when the bases were exchanged through the medium of 0.1 *N* $BaCl_2$ solution is 11.78; for the bases obtained by leaching with normal ammonium acetate solution, 11.67; and for the migration method, 3.73. This shows clearly the tendency for the migration method to extract a larger proportion of the alkali bases than is possible by other methods. At the same time the migration method extracted amounts of alkaline earth bases comparable to those obtained by the other methods. The fact that sodium is extracted so readily by the migration method and does not appear in the extracts in the leaching methods, is significant and seems to indicate a weakness in these methods, in so far as alkali soil studies or hardpan studies are concerned or any investigation of soils where the ratio of sodium and calcium is considered significant. For such studies the migration method is peculiarly suited.

The migration method also favors the extraction of magnesium, as is shown by the calcium-magnesium ratios in table 5. In all but one soil, more magnesium in proportion to calcium was obtained through the use of the migration method than by the other methods. From the physiological standpoint this should be significant, and if any relationships between replaceable bases and plant growth are to be established it would appear that the migration method would give a truer picture of the nutrient ratios than certain other methods. It seems strange that with a single treatment with normal ammonium acetate solution, followed by migration, larger amounts of both sodium and magnesium are usually obtained than can be liberated through leaching processes with the same solvent. It is possible, however, that the presence, in many cases, of excessive amounts of calcium which is dissolved directly from the soil forces back the reactions by which the magnesium and sodium are coming into solution. This would tend toward abnormally high calcium yields and a repression in magnesium and sodium yields, not because the latter elements are not in replaceable form, but because they are unable to go into solution in the presence of so much calcium. If the indications given by the use of the migration method are further substantiated, it would seem that the earlier pictures of the relationship between replaceable bases in the soil have not been entirely true, especially in calcareous soils.

Other possible applications of the migration method

In this study only the cations that migrate out of the soil have been investigated, but, by a suitable change in experimental procedure, it would be equally possible to study the anions. A slow moving, colored anion and a reversal of poles would enable the investigator to obtain data equally well for anion relationships. The relationship between soil bases and those absorbed by and present in the cells of plants could also be investigated by this method, by embedding ground plant tissue in agar and subjecting it to the usual migration procedure. Further studies along these lines are in progress.

SUMMARY

Three methods for the extraction of replaceable bases from soils have been compared on a group of 10 soils, 4 of which contain carbonates. The methods were the 0.1 *N* $BaCl_2$ leaching method of Burgess and Breazeale, the normal ammonium acetate leaching method of Chapman and Kelley, and a newly devised migration method for extraction after treatment of the soil with hot normal ammonium acetate solution.

The results of the comparative studies show a preferential extraction of alkaline earth bases over alkali bases in the case of the leaching methods, if the results obtained by migration procedure are considered as a basis for judgment. Since the migration method does not appreciably change the pH value of the soil during extraction, or bring about excessive solubilities through leaching, it seems to do away with the worst features of other methods, including electrodialysis.

The results of the migration method show that the present ideas, based upon leaching methods and others, regarding the ratios of replaceable bases in soils must be revised. There is generally more sodium and magnesium in replaceable form in the soils than has formerly been obtained through the use of the usual methods of extraction.

The significance of these newer relationships between exchangeable cation may more clearly show the reasons for the field behavior of soils and plants, especially in the drier climates, where carbonates often occur in the soils.

Use of the migration method may probably be made in connection with anion studies in soils and in the extraction of mineral constituents from plant tissues.

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ELECTRODIALYSIS AS A MEANS OF STUDYING THE NATURE OF SOIL PHOSPHATES[1]

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Recently, electrodialysis has come into use as a means of studying the solubility and availability of the nutrient elements of soils. Varying opinions are held as to its value for the study of the nature of soil phosphates, and it was the purpose of this investigation to obtain further information along this line.

For a review of the literature, the reader is referred to the recent articles of Harper (3), McGeorge (5), and Scarseth (7).

The variables, mechanism, and interpretation of electrodialysis are best understood by a consideration of Hyman's (4) mathematical expression for the rate of desalting of the center compartment of a three compartment electrodialysis cell. This expression shows that time, potential gradient, and nature and concentration of substance to be electrodialyzed are important factors that must be given due consideration in the interpretation of results. In his treatment of the subject he assumed that the following individual phenomena affect the desalting: dialysis, electrolysis, electro-endosmotic flow.

The expression given for the rate of desalting by electrodialysis is:

$$-\frac{dC}{dt} = \frac{q}{V} \times \frac{E}{F} \times \alpha(u + v)\, C \qquad (A)$$

where:

C = concentration of electrolyte within the membrane, expressed in millimoles.

t = time.

q = area of electrode.

V = volume of suspension in center compartment.

$E = \frac{e}{l}$; e = potential on electrodes, l = distance between electrodes.

F = 96,500 coulombs.

α = degree of dissociation.

$u + v$ = Hittorf's transference numbers.

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[2] The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Prof. E. Truog.

EXPERIMENTAL

Method of electrodialysis

Apparatus. The apparatus used was a cell of the type devised by Mattson (6). The dimensions of the graphite anode and of the copper gauze cathode were $5\frac{3}{4}$ by $3\frac{3}{4}$ inches. Both the anode and cathode membranes consisted of parchment paper. No attempt was made to eliminate the effect of the electric charge of the membrane.

Procedure. During the course of this investigation, two types of materials were electrodialyzed; namely, phosphate compounds and soils. In electrodialyzing soils, 100 gm. of 60-mesh soil and 100 cc. of water were stirred together to form a suspension, which was then immediately transferred to the center compartment of the cell. The two outside compartments were each filled with 225 cc. of distilled water, and the electrodes connected to a source of direct current giving 75 volts. During the electrodialysis the voltage was regulated so that it was constantly 75 volts, but the amperage was allowed to drop as the resistance of the cell increased. At approximately 1, 3, 6, 12, 24, 36, 48, and 60 hours, samples were taken by draining the liquid out of the two outside compartments. The phosphate content was determined in the anode liquid by taking an aliquot, adding 2 cc. of 10 per cent magnesium nitrate solution, evaporating to dryness, igniting, dissolving the residue, and determining the phosphate colorimetrically, using Truog and Meyer's (9) modification of Denigés' method. It was necessary to ignite because the graphite anode slowly decomposed, forming a colloidal solution of carbon. The cathode liquid was titrated with 0.1 *N* HCl in order to determine the total bases removed.

The electrodialysis of phosphate compounds was carried out by mixing a weighed sample with 100 cc. of water and then transferring the suspension to the center compartment of the cell. From this point, the procedure was the same as in the case of soils.

Electrodialysis of readily soluble phosphate compounds

Electrodialysis of tribasic calcium phosphates. In view of the fact that calcium is usually the dominant active base present in most soils, it was assumed that the calcium phosphates would be the most important of the readily soluble phosphate compounds. Therefore, two of the more insoluble calcium phosphates; namely, tricalcium and rock phosphates, were electrodialyzed in order to have some basis of comparison. The results of this test are shown in figure 1.

These curves show that the rate at which the phosphate was removed was dependent to some extent upon the original concentration of the material present in the center compartment. The last traces of the phosphate were removed at a much slower rate.

Electrodialysis of soils to which phosphates had been applied. Attention was next turned to determining the manner in which phosphate is removed from soils to which calcium phosphates had been added. For the purposes of this

study a set of soils from the University of Illinois experimental field at Aledo[3] were used. A summary of the results obtained on the electrodialysis of these soils is given in table 1. Electrodialysis reveals surprising differences in the effect of different treatments. In the cases of the superphosphate and rock phosphate plats a large percentage of the phosphate had been converted into a form which was not attacked by electrodialysis. However, in the case of the lime-rock phosphate plat, none of the applied phosphate had been converted into a form from which electrodialysis would not readily remove the phosphate.

The rate curves for the electrodialysis of these soils (fig. 2) show that a large portion of the phosphate is removed at a constant rate, as is indicated by the

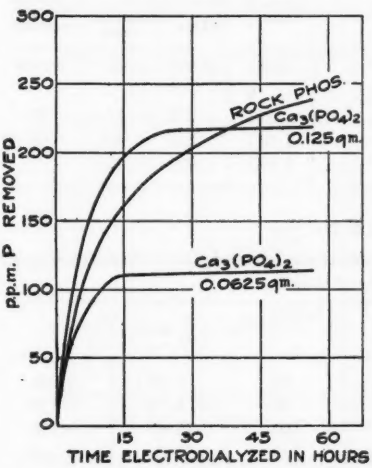

FIG. 1. RATES OF REMOVAL BY ELECTRODIALYSIS OF PHOSPHORUS FROM TRIBASIC CALCIUM PHOSPHATES AND ROCK PHOSPHATE

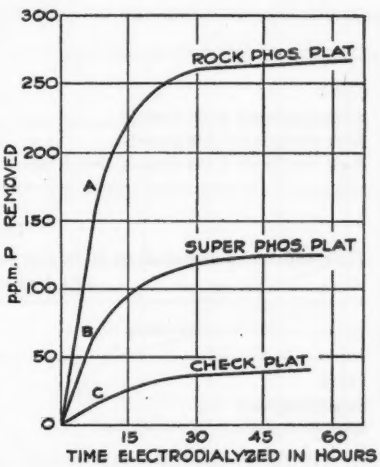

FIG. 2. RATES OF REMOVAL BY ELECTRODIALYSIS OF PHOSPHORUS FROM SOIL UNTREATED AND TREATED WITH CALCIUM PHOSPHATES

straight lines at the beginnings of the curves, i.e., OA, OB, OC. If these straight lines may be interpreted to mean that the same compound, for the most part, is being acted upon during the intervals of time which these straight lines represent, it becomes possible to calculate a specific electrodialysis constant. Assuming that the only variable is the original concentration of the compound, equation (*A*) may be written as follows:

$$-\frac{dC}{dt} = KC \qquad (B)$$

or

$$\text{slope} = KC \qquad (C)$$

[3] The writer is indebted to the University of Illinois for these samples, which were taken in the the fall of 1928 and kindly furnished by Mr. A. U. Thor.

Using the value of C represented by the points A, B, and C, the values of K were calculated. The results of these calculations are given in table 2. It may be deduced from these calculations that about 50 per cent of the phosphate applied as fertilizer to these soils is present in them in the same or a similar

TABLE 1

Removal of phosphorus during 50 hours of electrodialysis from soils of variously treated plats of Aledo experimental field, University of Illinois

TREATMENT	PHOSPHORUS APPLIED PER ACRE (APPROXIMATE)	PHOSPHORUS PER ACRE REMOVED BY ELECTRODIALYSIS		APPLIED PHOSPHORUS NOT RECOVERED BY ELECTRODIALYSIS
		Total	Total less check	
	pounds	*pounds*	*pounds*	*per cent*
Check	0	77	....	..
Superphosphate 4,066 pounds	293	250	173	59
Rock phosphate 8,334 pounds	1,042	526	449	43
Rock phosphate 8,334 pounds, lime 6 tons	1,042	1,202	1,125	..

TABLE 2

The specific rate of electrodialysis, K, for soils from the variously treated plats of Aledo experimental field, University of Illinois

TREATMENT	c	$-\frac{dC}{di}$ SLOPE	K
Check	25	2.05	0.082
Superphosphate	70	8.24	0.118
Rock phosphate	170	20.0	0.118
Rock phosphate and lime	425	50.0	0.118

form, and that none of the phosphate in the check plat is in as soluble a form as this.

Electrodialysis of difficultly soluble phosphate compounds

Electrodialysis of iron and aluminum phosphates. What is the effect of electrodialysis upon difficultly soluble phosphate compounds? For the purposes of this study, samples[4] of ferric phosphate, aluminum phosphate, and dufrenite [$Fe_2(OH)_3PO_4$] each containing 0.025 gm. of phosphorus were electrodialyzed. The results are shown graphically in figure 3. It may be seen from these curves that the compounds contained slight amounts of easily soluble phosphate as impurities as indicated by the curved part at the beginning. After these impurities were removed, the rate curves became straight lines except in the case of the ferric phosphate, which had a break in the straight line. In view of the fact that the original amount of phosphorus was the same in all cases, the

[4] The ferric and aluminum phosphates used were prepared in this laboratory by Mr. L. M. Weyker. They were considerably purer than ordinary commercial products obtainable.

slopes of the straight lines bear a simple relation to the rate of solution or hydrolysis of these compounds. It was noted that when the iron phosphates were being electrodialyzed, no iron was detected in the cathode compartment.

Electrodialysis of soils containing only difficultly soluble phosphates. For the purposes of this study two stock soils from the Experiment Station of the Association of Hawaiian Pineapple Canners were used. These soils are distinctly lateritic and contain a normal amount of total phosphorus which is practically all in difficultly soluble form. The results of the electrodialysis of these soils are shown in figure 4. The only generalization that can be drawn from these curves is that in the electrodialysis of soils of this type under these conditions, the rate of removal of phosphate from the iron and aluminum phosphates is

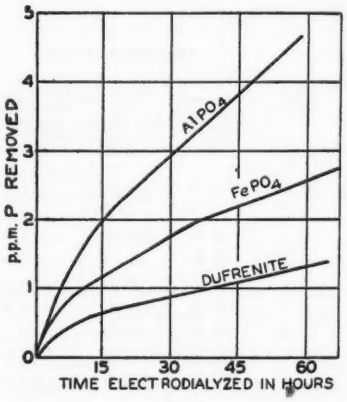

FIG. 3. RATES OF REMOVAL BY ELECTRODIALYSIS OF PHOSPHORUS FROM DIFFICULTLY SOLUBLE PHOSPHATE COMPOUNDS

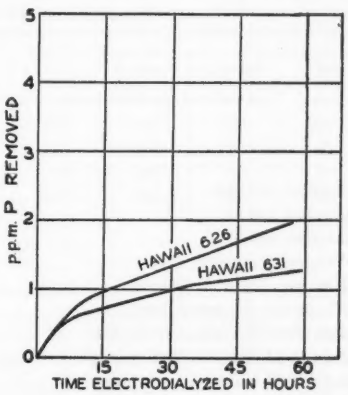

FIG. 4. RATES OF REMOVAL BY ELECTRODIALYSIS OF PHOSPHORUS FROM SOILS CONTAINING DIFFICULTLY SOLUBLE PHOSPHATE COMPOUNDS

extremely slow. It may be noted that in the electrodialysis of soils containing only difficultly soluble phosphates, the curves obtained are similar to those obtained with iron phosphates.

The total quantity of phosphate removed from soils by electrodialysis

A comparison of the total quantity of phosphate removed by electrodialysis and by three successive extractions, using a modification[5] of Truog's (8) method of determining readily soluble phosphorus is given in table 3. These data reveal a fairly good agreement between the amounts of phosphorus removed by electrodialysis and by three extractions with 0.002 N H_2SO_4. However, a

[5] The modification being that the ratio of soil to extracting solution was changed from 1 to 200 to 1 to 400.

critical examination shows that the soils may be divided into the following three classes:

Soils from which more phosphate is removed by acid extraction than by electrodialysis.
Soils giving a good agreement between the two methods.
Soils from which more phosphate is removed by electrodialysis than by acid extraction.

Soils from which more phosphate is removed by acid extraction than by electrodialysis. The lateritic soils of Hawaii, as far as studied, fall in the first class and are peculiar in that acid extraction removed more phosphorus than did

TABLE 3

A comparison of the amounts of phosphorus removed from soils by electrodialysis for 60 hours, and by extractions with 0.002 N H_2SO_4 of pH 3

DESCRIPTION OR SOURCE OF SOIL	pH OF SOIL	P.P.M. OF PHOSPHORUS		
		Removed by electrodialysis for 60 hours	Removed by 3 extractions with 0.002 N H_2SO_4	Amount by electrodialysis less amounts by extraction
Hawaiian soil 626	4.6	1.97	9.0*	−7.03
Hawaiian soil 631	4.4	1.28	9.0*	−7.72
Hawaiian soil 4391	6.3	50.0	376.0	−228.0
(Wisconsin) Superior clay	5.2	42.0	59.0	−17.0
(Wisconsin) Miami silt loam	5.8	9.2	28.0	−19.0
(Wisconsin) Miami silt loam	6.7	96.0	112.0	−16.0
Aledo Field (Illinois), check plat	5.0	39.0	41.0	−2.0
Aledo Field (Illinois), superphosphate plat	5.0	125.0	112.0	+13.0
Aledo Field (Illinois), rock phosphate plat	5.5	263.0	259.0	+4.0
Aledo Field (Illinois) lime and rock phosphate plat	6.0	601.0	599.0	+2.0
Montana soil	8.1	169.0	179.0	−10.0
Wyoming soil	7.5	199.0	114.0	+85.0
Idaho 10622	7.6	476.0	414.0†	+62.0
Idaho 10626	8.3	575.0	504.0†	+71.0

* One extraction.
† Five extractions.

electrodialysis. A few of the middle western soils showed the same type of variation to a limited extent. The results obtained thus far lead one to believe that electrodialysis attacks calcium phosphates readily and iron and aluminum phosphates only sparingly. Consequently, it was assumed that acid extraction attacked difficultly soluble phosphates more readily than did electrodialysis.

In order to obtain a definite idea of the effect of 0.002 N H_2SO_4 at pH 3 on iron and aluminum phosphates, 0.5-gm. samples were treated in exactly the same manner as 0.5-gm. soil samples were treated, the extraction method according to Truog (8) being used. The results of five successive extractions are shown in table 4. These results show that the ferric phosphate, dufrenite,

and soil 4391 were affected in somewhat the same manner with respect to removal of phosphate by the acid extractions, whereas the aluminum phosphate seemed to be affected in a somewhat different manner. These results have led to the belief that at pH 3, aluminum phosphate goes into solution, forming two soluble compounds; namely, aluminum sulfate and phosphoric acid, whereas the ferric phosphate forms one soluble and one less soluble compound; namely, phosphoric acid and a basic iron phosphate.

TABLE 4

A comparison of the amounts of phosphorus dissolved in successive extractions with 0.002 N H_2SO_4 *of pH 3 from 0.5-gm. samples of difficulily soluble phosphate compounds and one soil*

MATERIAL	P.P.M. PHOSPHORUS REMOVED BY EXTRACTION WITH 0.002 *N* H_2SO_4				
	In first extraction	In second extraction	In third extraction	In fourth extraction	In fifth extraction
$AlPO_4$	700	820	600	670	540
$FePO_4$	260	160	92	80	68
Dufrenite	200	98	80	60	56
Hawaiian Soil 4391	180	120	76	68	54

TABLE 5

The amounts of phosphorus removed in successive extractions with 0.002 N H_2SO_4 *of pH 3 from goethite treated with varying quantities of a soluble phosphate* (KH_2PO_4)

P.P.M. PHOSPHORUS ADDED TO 0.5 GM. SAMPLES OF GOETHITE	P.P.M. OF PHOSPHORUS REMOVED IN SUCCESSIVE EXTRACTIONS WITH 0.002 *N* H_2SO_4				PER CENT NOT REMOVED
	In first extraction*	In second extraction	In third extraction	In fourth extraction	
200	30	18	14	14	62
500	36	29	25	21	78
1,000	61	44	34	33	83
2,000	420	124	100	56	65
3,000	860	176	124	70	59
4,000	1,520	204	132	70	52
5,000	1,840	256	160	80	53

* The first extraction contained some soluble phosphate left by the treatment.

If it is possible to obtain, by successive extractions, ferric phosphates which have decreasing solubilities, it should be possible to do the reverse, and build up phosphate compounds having increasing solubilities. Consequently, 0.5-gm. samples of Goethite ($Fe_2O_3 \cdot H_2O$) were treated with increasing amounts of monobasic potassium phosphate (KH_2PO_4) and 50 cc. of water, and allowed to go to dryness on the steam plate. These samples were then extracted with 0.002 *N* H_2SO_4. The results are given in table 5. In considering these data, the results obtained with the first extraction should be eliminated because some

of the phosphate removed was not derived from iron phosphates formed but from KH_2PO_4 that had not reacted. The remaining results clearly show that a series of compounds with increasing solubilities had been formed.

In order to obtain further evidence of the nature of the phosphate present in soil 4391, a comparison of the rate of electrodialysis of this soil and of iron and aluminum phosphates was made. This is shown in figure 5. The curves for the iron and aluminum phosphates in figure 5 are based upon the data given in figure 3, and were calculated in the following manner: Since the curves given in figure 3 were obtained by the electrodialysis of samples containing 0.025 gm. of phosphorus whereas the sample of soil 4391 which was electrodialyzed contained 1.35 gm. of phosphorus, by simple proportion the slopes of the lines

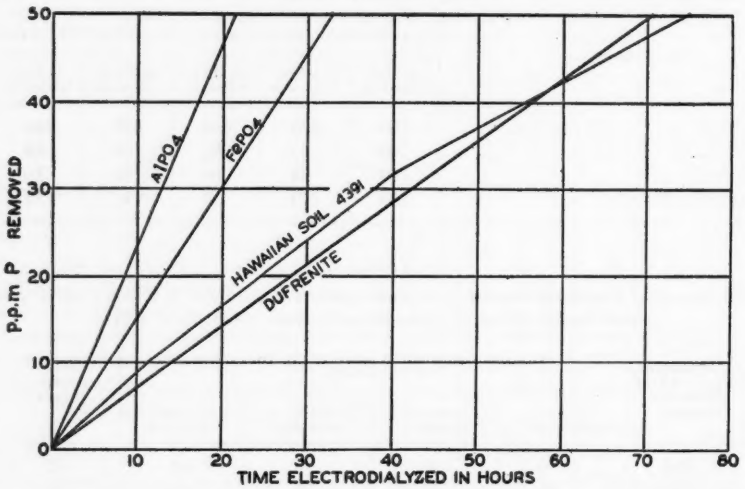

FIG. 5. A COMPARISON OF THE RATES OF REMOVAL OF PHOSPHORUS BY ELECTRODIALYSIS FROM HAWAIIAN SOIL 4391 AND FROM IRON AND ALUMINUM PHOSPHATES, ALL SAMPLES CONTAINING EQUAL QUANTITIES OF PHOSPHORUS

for the electrodialysis of samples of iron and aluminum phosphates, each containing 1.35 gm. of phosphorus, were calculated and expressed graphically as shown. These curves show that there is a marked similarity between the electrodialysis curves for soil 4391 and dufrenite.

In view of the fact that soil 4391 and dufrenite show a marked similarity in their behavior when they are either electrodialyzed or extracted with acid, it is believed that the main body of the phosphate present in this soil is in the form of dufrenite or in a form similar thereto. Also, it may be concluded that when more phosphate is removed from a soil by acid extraction than by electrodialysis for 60 hours under the conditions described, most of the phosphate present in that soil is in the form of iron phosphates.

Soils giving a good agreement between the amounts of phosphate removed by

electrodialysis and acid extraction. In the second class fall those soils from the humid temperate regions which contain a fair quantity of readily soluble phosphate. Data previously presented show that electrodialysis will remove this form of phosphate quite readily from soils. Consequently, when this type of soil is being dealt with, both methods appear to be equally satisfactory.

Soils from which more phosphate is removed by electrodialysis than by acid extraction. In the third class fall the calcareous or alkaline soils derived from the arid regions of the western part of the United States. On first consideration it might be thought that the reason for the difference found here might be

TABLE 6

The amounts of phosphorus extracted by 0.002 N H_2SO_4 of pH 3 from soils after being electrodialyzed for 60 hours, compared with the amounts extracted from the original soils in the third of successive extractions

DESCRIPTION OR SOURCE OF SOIL	P.P.M. PHOSPHORUS EXTRACTED BY 0.002 *N* H_2SO_4	
	In first extraction of electrodialyzed soil	In third successive extraction of original soil
Hawaiian soil 626	8.0	...*
Hawaiian soil 631	9.0	...*
Hawaiian soil 4391	170.0	76.0
Superior clay—Wisconsin	21.0	11.0
Miami silt loam—Wisconsin	13.0	5.6
Miami silt loam—Wisconsin	18.0	12.0
Aledo Field, Ill.—Check plat	17.6	9.6
Aledo Field, Ill.—Superphosphate plat	18.0	16.0
Aledo Field, Ill.—Rock phosphate plat	24.0	32.8
Aledo Field, Ill.—Lime and rock phosphate plat	30.0	52.6
Montana soil	46.0	27.0
Wyoming soil	17.6	22.0
Idaho soil 10622	24.0	13.0†
Idaho soil 10626	52.0	34.0†

* Not determined.

† Fifth extraction.

due to the calcium carbonate neutralizing the acid which was used for extraction. However, a study of the pH of the various acid extracts showed that in the case of the soils studied, only the pH of the first extract was affected. Because three to five acid extractions were made on these soils, it is believed that the neutralization of the acid by the calcium carbonate is not a plausible explanation of the differences obtained. Scarseth (7) also found that when calcareous soils are electrodialyzed, large amounts of phosphorus are removed.

The phosphorus-containing organic compounds of soils have not been thoroughly studied. It is here suggested that under alkaline soil conditions there may be organic compounds present in soils which yield phosphorus by electrodialysis but not by acid extraction.

The nature of the difficultly soluble phosphates present in soils

Phosphates remaining in soils electrodialyzed for 60 hours or extracted with acid. The soils which had been electrodialyzed for 60 hours to remove the readily soluble phosphate were dried at 40°C., pulverized to pass a 60-mesh sieve, and the solubility of the phosphate present was determined by extraction with 0.002 *N* H_2SO_4. The results of these determinations are given in table 6. The solubilities of the phosphate in practically all of the soils studied are of the same order. This would tend to indicate that the difficultly soluble phosphates in

TABLE 7

Amounts of phosphorus recovered by extraction of soils and materials with 0.002 N H_2SO_4 of pH 3 after these materials had been treated with 500 p.p.m. of phosphorus in form of KH_2PO_4

SOIL OR MATERIAL TO WHICH 500 P.P.M. PHOSPHORUS WAS ADDED	P.P.M. PHOSPHORUS EXTRACTED BY 0.002 *N* H_2SO_4				PER CENT APPLIED PHOSPHORUS NOT RECOVERED IN FOUR EXTRACTIONS
	In first extraction	In second extraction	In third extraction	In fourth extraction	
Superior clay—after electrodialysis	260	48	38	22	26.4
Miami silt loam—after electrodialysis	300	50	44	22	16.8
Miami silt loam—after electrodialysis	200	58	28	18	39.6
Montana soil—after electrodialysis	330	60	33	18	11.8
Aledo Field, Ill.—after electrodialysis	290	68	47	22	14.6
Idaho 10622—after electrodialysis	320	62	45	22	10.2
Hawaiian soil 631	52	24	18	17	77.8
Hawaiian soil 626	30	17	13	13	84.4
Hawaiian soil 555	56	35	24	18	73.4
Hawaiian soil 1591	112	54	41	30	52.6
Hawaiian soil 1594	72	35	26	19	69.6
Hawaiian soil 3128	114	56	35	32	52.6
Limonite	74	40	24	24	67.6
Goethite	36	29	25	21	77.8

all of these soils were of a similar nature. Samples of the same soils which had not been electrodialyzed were subjected to a series of acid extractions, and the amounts of phosphate removed in the third extraction are given in table 6. In a general way these results are similar to those obtained after electrodialysis.

Nature of the phosphates formed when a soluble phosphate is added to soils and minerals. It has been noted that when soluble phosphates are added to soils, varying quantities of the phosphate are converted into difficultly soluble forms. In order to determine whether compounds formed in this manner were similar to those present in soils after the soils had been electrodialyzed, the following test was carried out. Half-gram samples of soil, which contained no readily soluble phosphates, were treated with 50 cc. of a solution containing 5 p.p.m. of phosphorus, and the suspension was allowed to go to dryness on the steam plate. This application is equivalent to adding 500 p.p.m. of phosphorus to

the soil. The soil was then subjected to a series of extractions with 0.002 *N* H_2SO_4 at pH 3. The results of these extractions are given in table 7 and show that when phosphate is added to a soil a portion of it is converted into an insoluble form which seems to be similar in all the soils studied. They also show that the two hydrated iron oxides reacted in a similar manner. These results are in accordance with those reported by Ford (1).

Do any other compounds present in soils besides the hydrated iron compounds form difficultly soluble phosphates? Fraps (2) reported that various other soil minerals fix phosphorus. In order to obtain further information on this subject, a large variety of substances which were ground to pass a 100-mesh sieve, were

TABLE 8

The amounts of phosphorus removed and not removed from various minerals and materials by extraction with 0.002 N H_2SO_4 *of pH 3, after treatment with 500 p.p.m. of phosphorus in the form of* KH_2PO_4

MINERAL OR MATERIAL TREATED AND EXTRACTED	P.P.M. OF PHOSPHORUS REMOVED BY EXTRACTION WITH 0.002 *N* H_2SO_4				P.P.M. PHOSPHORUS NOT RECOVERED
	In first extraction	In second extraction	In third extraction	In fourth extraction	
Anorthoclase	700	160	48	8	0
Talc	530	0	..	..	0
Apophyllite	580	88	32	18	0
Nontronite	520	104	16	..	0
Red Granite	500	68	48	38	0
Kaolin	400	88	22	..	0
Muscovite	270	180	92	30	0
Biotite	288	112	56	15	29
Microcline	460	0	0	..	40
Orthoclase	420	20	0	..	60
Albite	425	0	0	..	75
Stilbite	412	0	0	..	88
Ca saturated Doucil	22	8	14	26	430
Meta Titanic Acid $TiO(OH)_2$	0	0	0	..	500
Ortho Titanic Acid $Ti(OH)_2$	0	0	0	..	500

treated with solutions of monobasic potassium phosphate (KH_2PO_4) in the manner previously described. The results are given in table 8. These data indicate that there is a large variety of substances which have the ability to combine with phosphates, to a limited extent, forming difficultly soluble compounds. Of the substances listed, the titanic acids, which were prepared in this laboratory, and Doucil, which is a commercial zeolite used as a water softner, fixed phosphate to the greatest extent. In view of the fact that the presence of alumino silicates of this type in soils is doubtful, it is believed that this latter class of substances would have little bearing on the phosphate fixation in soils. Generally speaking, soils contain only about 0.5 per cent of TiO_2, which is hardly sufficient to be of importance in comparison with the relatively large

amounts of hydrated iron oxides commonly present. However, data such as those presented in table 9 would suggest that in some soils titanium might be an important factor in phosphate fixation.

TABLE 9

*The total amount of titanium oxide in Hawaiian soils from different islands of the group**

SOIL NUMBER	LOCATION	PER CENT TiO_2
626	Kauai	7.51
631	Maui	11.37
913	Hawaii	3.69
917	Oahu	3.53
920	Molokai	15.53

* The writer is indebted to Dr. O. C. Magistad of the Experiment Station of the Association of Hawaiian Pineapple Canners, University of Hawaii, for data presented in this table.

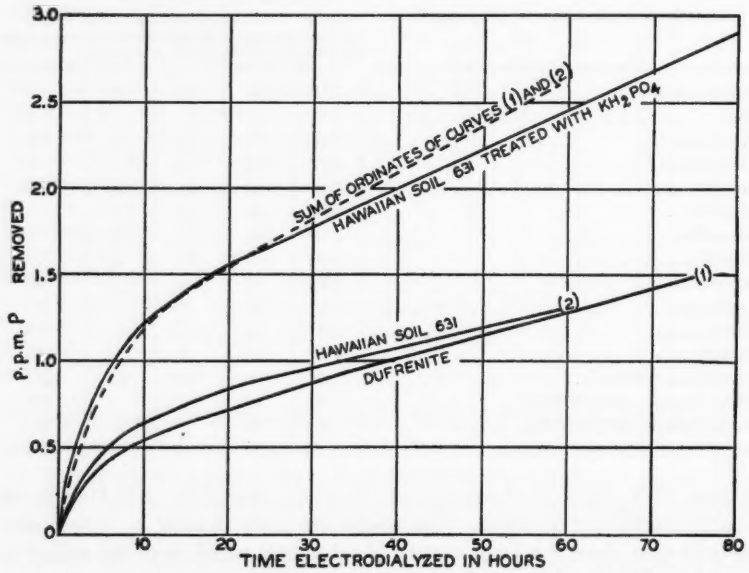

FIG. 6. RATE OF REMOVAL OF PHOSPHORUS BY ELECTRODIALYSIS FROM A TREATED AND AN UNTREATED SOIL AND FROM DUFRENITE. ALSO A CURVE BASED ON THE SUM OF THE CORRESPONDING ORDINATES OF THE TWO LOWER CURVES

In order to obtain further insight as to the nature of the difficultly soluble phosphates formed in soils, the rate of electrodialysis of a soil, which had received an application of phosphate, was studied. A 100-gm. sample of Hawaiian soil 631, 100 cc. of water, and 0.025 gm. of phosphorus in the form of

KH_2PO_4 were stirred together to form a suspension and then dried at 60°C. More water was added, and the suspension dried for a second time. The dried soil was then electrodialyzed in the usual manner. The results are shown in figure 6.

If the phosphorus added was converted into a compound similar to dufrenite, then the ordinates of the curve for the electrodialysis of 100 gm. of untreated Hawaiian soil 631, added to the corresponding ordinates of the curve for the electrodialysis of a sample of dufrenite containing 0.025 gm. of phosphorus, should be the same as the curve given for the electrodialysis of the soil sample to which 0.025 gm. of phosphorus had been added. Figure 6 shows that such is the case. It is, therefore, reasonable to infer that when a soluble phosphate is added to some soils, basic iron phosphates, similar to dufrenite, are formed. Ford (1) came to a similar conclusion.

SUMMARY

In a study of electrodialysis as a means of determining the nature of soil phosphates, the following points were covered: (*a*) the electrodialysis of readily soluble phosphate compounds; (*b*) the electrodialysis of difficultly soluble phosphate compounds; (*c*) the total quantity of phosphate removed by electrodialysis as compared to that removed by Truog's method of acid extraction; and (*d*) the nature of the difficultly soluble phosphates present in soils. The results of this study may be summarized as follows:

Either electrodialysis or extraction with acid removes readily soluble phosphate compounds from soils.

Electrodialysis does not remove phosphate from iron phosphates of soils nearly so rapidly as do extractions with 0.002 *N* H_2SO_4.

Electrodialysis for 60 hours removes more phosphate from some calcareous soils than do five extractions with 0.002 *N* H_2SO_4.

The difficultly soluble phosphate compounds of all the soils studied seemed to be similar, as revealed by deportment to electrodialysis and acid extractions.

The difficultly soluble phosphates formed by adding soluble phosphate to hydrated iron oxides appear to be similar to the difficultly soluble phosphates present in soils.

The phosphate naturally present in a lateritic soil containing 1.35 per cent phosphorus was similar in solubility to dufrenite.

The difficultly soluble phosphate compounds formed by the addition of soluble phosphate to some soils appears to be similar to dufrenite.

Under limited conditions, the specific rate of removal of phosphate from soils by electrodialysis may be used advantageously as an index of identification of the nature of the phosphate compounds present.

The determination of readily soluble phosphorus for practical purposes can be made not only more quickly and economically by acid extraction than by electrodialysis, but also with greater dependability.

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THE FIXATION OF POTASH IN DIFFICULTLY AVAILABLE FORM IN SOILS[1]

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Numerous workers have shown that when soluble potash salts are applied to soils, the potassium is usually taken up quickly by the exchange material and held in exchangeable or readily available form, thus preventing serious loss in the drainage water (13). In time, a large portion of this exchangeable potassium is apparently transformed to a non-exchangeable and difficultly available form (5, 7, 22), the nature of which has, as yet, not been clearly elucidated.

Many years ago Dyer (5), at Rothamsted, worked with the soil of the Hoos Field, one plat of which had received 4,084 pounds per acre of potash over a period of 38 years. The potash removed by the crops and that remaining soluble in 1 per cent citric acid accounted for only about one-half of this amount, the remainder having either been leached away or converted into difficultly soluble forms. The latter explanation appears more plausible, since in five different groups of plats in the same field where potash plats and check plats could be compared, the treated plats invariably contained sufficient amounts of total potash to account for that applied.

About 25 years later Frear and Erb (7), working with the Pennsylvania Soil Fertility Plats, determined the potash content of a check plat and of one which had received 200 pounds per acre of potassium chloride biennially for 36 years (1881–1916), making in all a total of 1,793 pounds per acre of potash. Here again, as in the case of the Hoos Field, only about one-half of this potash was accounted for by that removed by the crops and remaining in the soil in readily available forms.

The present paper reports the results of an investigation of the nature of potash fixation in soils.

EXPERIMENTAL

As already indicated, potash fixation may be of two kinds; namely, fixation as replaceable or readily available potash, and fixation as non-replaceable or

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difficultly available potash. In order to facilitate discussion, the expression "potash fixation" will be used in this paper in a restricted sense to include only the latter form of fixation.

In the experiments that follow, the readily available potash was extracted from the soil with a normal solution of ammonium acetate, and the analytical determinations of potassium were made by the permanganate titration of the cobalti-nitrite salt, as described elsewhere (30, 31).

TABLE 1

Influence of wetting and drying soils in different ways on the fixation of potash added at the rate of 1,000 pounds per acre in the form of the chloride

TEST NUMBER	TREATMENT OF THE SOILS AS REGARDS WETTING, DRYING, AND PERIOD OF INCUBATION	POUNDS PER ACRE OF POTASH FIXED	
		Miami silt loam	Hagerstown silt loam
1	Stood as water suspension for 5 minutes	0	0
2	Stood as water suspension for 1 day	0	0
3	Stood as water suspension for 5 days	0	0
4	Stood as water suspension for 10 days	0	0
5	Stood as wet paste for 5 minutes	0	0
6	Wet paste allowed to dry at room temperature 16 hours. Still very wet	0	0
7	Wet paste allowed to dry at room temperature 40 hours. Still moderately wet	0	0
8	Wet paste allowed to dry at room temperature 90 hours. Nearly dry	60	32
9	Wet paste allowed to dry at room temperature 125 hours. Completely air dry	300	252
10	Soil wetted and dried once at 70°C.	372	320
11	Soil wetted and dried 2 times at 70°C.	392	340
12	Soil wetted and dried 4 times at 70°C.	428	362
13	Soil wetted and dried 8 times at 70°C.	440	384
14	Soil wetted and dried 16 times at 70°C.	464	396
15	Soil wetted and dried 24 times at 70°C.	476	424
16	Soil wetted and dried 32 times at 70°C.	488	428

Conditions favoring potash fixation in soils

Preliminary tests revealed that potassium in the form of soluble salts is not fixed by soils to a great extent from dilute solutions unless drying of the soil takes place. Tests were therefore undertaken to show the influence of moisture supply and wetting and drying of the soil on the fixation of potassium.

Two soils, Miami silt loam and Hagerstown silt loam, were used for the study. Twenty-five-gram portions of soil were placed in 500-cc. Erlenmeyer flasks, to each of which was added 35 cc. of water containing sufficient potassium chloride to equal an application of 1,000 pounds per acre of potash. In some cases the available potash of the soils in the flasks was immediately extracted with

500 cc. of normal ammonium acetate; in other cases the soils with added water were allowed to stand for several days; in others they were allowed to dry slowly; and in still others they were alternately wetted and dried at 70°C. several times before being extracted with normal ammonium acetate. The details of the treatments and the results are given in table 1. It is evident that little or no potash fixation occurred until drying began to take place, and that repeated wetting and drying increased the amount of fixation. For the two soils studied, approximately 75 per cent of the potash fixation took place with one drying at 70°C. as compared with that after 32 wettings and dryings at 70°C.

TABLE 2

Influence of continuous moistness versus alternate wetting and drying on the amount of potash fixed by a Miami silt loam treated with 10 tons per acre of potash as the bicarbonate

The soil contained 2.14 per cent of total potash before treatment

NUMBER OF TEST	TREATMENT OF SOIL AFTER ADDITION OF POTASSIUM BICARBONATE	PERCENTAGE OF TOTAL POTASH IN THE SOIL AFTER REMOVAL OF ALL THAT IS SOLUBLE AND REPLACEABLE	POUNDS PER ACRE OF POTASH FIXED BY THE SOIL	PERCENTAGE OF ADDED POTASH MIXED
1	Soil-water ratio made 1 to 3 and stood for 3 days	2.14	0	0
2	Optimum moisture conditions for 3 days	2.13	0	0
3	Soil moistened and allowed to dry slowly at room temperature for 3 days	2.20	1,200	6
4	Soil moistened and dried at once at 60°C.	2.32	3,600	18
5	Soil alternately wetted and dried 3 times at 60°C.	2.38	4,980	25
6	Soil alternately wetted and dried 6 times at 60°C.	2.40	5,388	27

To test further whether or not potash fixation would occur under moist conditions, 30-gm. portions of Miami silt loam and of Hagerstown silt loam were placed in carbon filter funnels and leached at the rate of 2 cc. per hour for 60 consecutive days with a solution containing 40 p.p.m. of potassium as the bicarbonate. Subsequent analyses showed that no appreciable amount of potassium had been fixed in a difficultly soluble form.

Since the effect of drying may be only that of concentration of the potassium salts, and thus subsequently due to mass action, more of the potassium is caused to go into difficultly available forms, a second set of tests was conducted to determine whether or not fixation would occur from concentrated solutions without the drying process. Miami silt loam was treated with potash in the form of the bicarbonate at the rate of 10 tons per acre. Portions of the treated and moistened soil were placed in test tubes and subjected to the various wet-

ting and drying treatments described in table 2. After treatment, the soils in the test tubes were completely freed of soluble and replaceable potash and analyzed for the total potash remaining in the soil. The differences in total potash between the treated and untreated portions of the soil give the amounts fixed. These results (table 2) substantiate those of the first set of tests; i.e., little or no fixation occurs until drying takes place.

There appeared to be a remote possibility that the potassium salts are held mechanically as inclusions in the partially dehydrated colloids of the soil, and

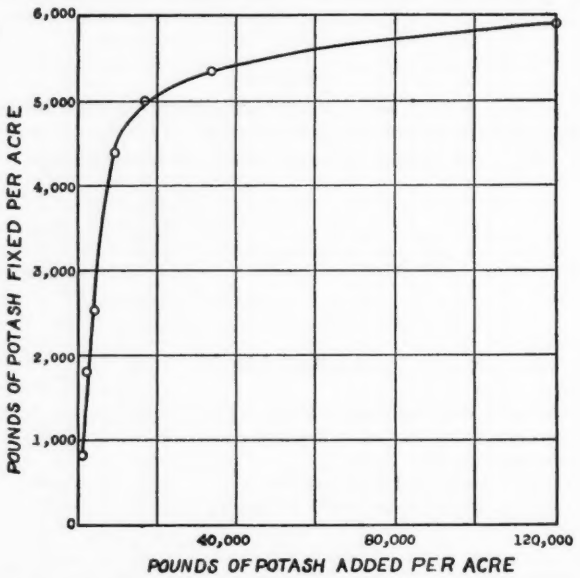

FIG. 1. EFFECT OF THE CONCENTRATION OF SOLUBLE POTASH ON THE AMOUNT FIXED BY MIAMI SILT LOAM WHEN TREATED WITH VARYING QUANTITIES OF POTASSIUM BICARBONATE AND THEN ALTERNATELY WETTED AND DRIED 10 TIMES AT 70°C.

that the potash is not actually fixed chemically. To test this, a synthetic soil was made, using the proper proportions of different sizes of quartz sand, together with silica gel so as to fit the results of a mechanical analysis of Miami silt loam. To this synthetic soil was added 10 tons per acre of potash as the bicarbonate, and the whole wetted and dried 10 times at 70°C. The dried material was found to retain no appreciable amount of potash.

Thus it appears that drying causes the formation of a potash-containing secondary mineral from which the potash is not brought into solution by water or ammonium acetate solution. Further evidence substantiating this theory will be given later.

Effect of the concentration of soluble potassium on fixation

In order to test the effect of the concentration of soluble potassium on the rate of fixation, eight 20-gm. portions of Miami silt loam were placed in test tubes and treated with 0, 1,000, 2,000, 4,000, 8,000, 16,000, 32,000, and 120,000 pounds per acre of potash as the bicarbonate respectively. The contents of each test tube were then wetted and dried 10 times at 70°C. The samples were

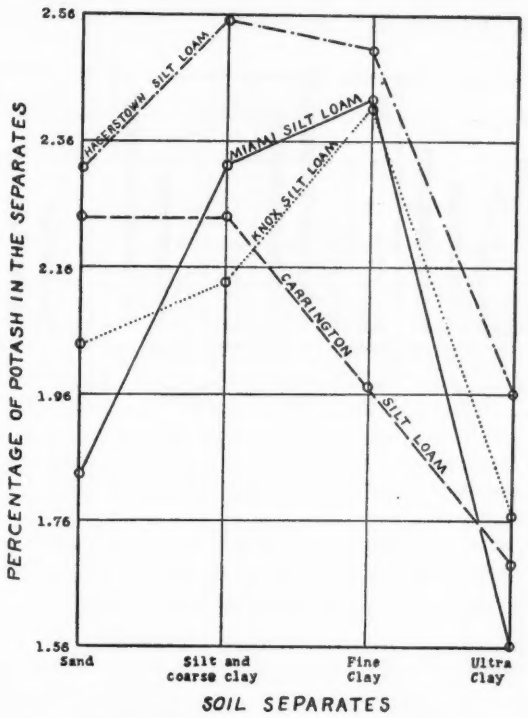

FIG. 2. POTASH CONTENT OF THE TEXTURAL SEPARATES OF FOUR SOILS

next leached with normal ammonium acetate to free them of readily available potassium, and then analyzed for total potash. The results of the analyses, given in graphical form in figure 1, show that the amount of potash fixed increased rapidly from an application of 1,000 pounds to 16,000 pounds, and that beyond an application of 32,000 pounds, very little increase in fixation took place. Approximately 80 per cent of the 1,000-pound application was fixed, and only 17 per cent of the 32,000-pound application. Thus, it appears that under the conditions of the experiment a soil will fix a maximum of potash in a very short time.

Soil separates as regards total potash and fixation

Several workers have shown that the potash content of a soil is not constant for its different mechanical separates. Soils investigated by Dumont (3) contained, in one case, five-sixths of the potash in the fine material, and one-sixth in the sands; and in another case, three-tenths in the fine material, and seven-tenths in the coarse. Steinkoenig (28) found that the potash content increased with fineness, and Gericke (9) found it concentrated in the particles ranging from 0.02 mm. to 0.002 mm. in diameter.

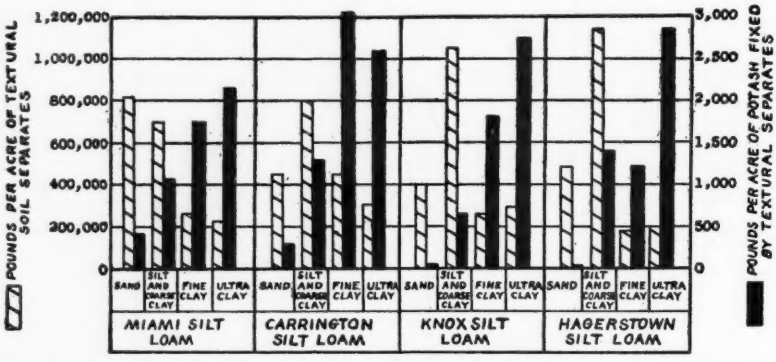

FIG. 3. AMOUNTS OF POTASH PER ACRE FIXED IN DIFFICULTLY AVAILABLE FORM BY THE TEXTURAL SEPARATES OF FOUR SOILS TREATED WITH 60 TONS PER ACRE OF POTASH AND ALTERNATELY WETTED AND DRIED 10 TIMES AT 70°C.

Four soils were simultaneously separated into four textural separates by centrifuging, and the resultant separates analyzed for total potash. The approximate diameters of the particles in the separates were:

Sands	>0.05 mm.
Silt and coarse clay	<0.05 mm. and >0.002 mm.
Fine clay	<0.002 mm. and >0.0003 mm.
Ultra clay	<0.0003 mm.

The data presented graphically in figure 2 show that for the four soils studied, the ultra clay separates have the lowest percentage of total potash, the sands the next lowest percentage, and the intermediate separates have the highest. These results suggest that the sand separates contain the greatest percentage of primary quartz, the medium sized separates contain the greatest percentage of feldspars, and the ultra clay consists mainly of secondary minerals containing less potash as a whole. The natural question arising at this point is: What separate exercises the greatest fixing power for potash?

Using the same four soils, another experiment was conducted in which two 40-gm. portions of each soil were placed in beakers. One of each pair was treated with 60 tons per acre of potash as the bicarbonate, and all were wetted

and dried 10 times at 70°C. The soils, treated and untreated, were then dispersed and leached as free as possible of soluble and replaceable potash by normal ammonium acetate, placed in centrifuge tubes and separated into four textural separates as previously described. Results of analyses for total potash are shown graphically in figure 3. In every case it will be noted that the ultra-clay is the highest fixer, fine clay next, and so on to the sand, where practically no fixation took place. The slight fixation by the coarse separates is attributed to the colloidal material that adhered to the surface of the grains and could be easily seen with a microscope. By taking a small portion of this coarse material and removing the colloidal material by rubbing, it was possible to reduce the treated and untreated coarse separates to nearly identical percentages of total potash. The specific fixing power of the soil separates of the four soils was calculated as follows: $\frac{\text{Weight of potash fixed}}{\text{Weight of separate}} \times 10{,}000 = \text{specific fixing power.}$ These calculations gave the results that follow: sand, 0 to 6; silt and coarse clay, 6 to 16; fine clay, 66 to 69; ultra clay, 82 to 140.

Capacity of various soils to fix added potash

Before attempting to determine the identity of the substances in soils causing potash fixation, a large number of soils were studied for their capacity to fix potash. One hundred samples, obtained from various parth of the United States, Hawaii, and Central America, were studied. Samples of the soils were placed in 500-cc. Erlenmeyer flasks, moistened with a solution of potassium chloride equivalent to 1,000 pounds per acre of potash, and immediately extracted with normal ammonium acetate. The potash was determined in the extract. A second set of samples, similarly treated with potash, were wetted and dried alternately 10 times on a hot plate at 70°C. and then extracted with normal ammonium acetate as before. The difference between the potash content of the extracts of the two sets of tests gives the amounts of potash fixed by the soils. The results given in table 3 show that fixation varies from 0 to 114 per cent of the 1,000 pounds added. The seven soils which ran over 100 per cent apparently fixed not only the 1000 pounds added, but some of the available potash originally present in them.

As a rule, the lower the colloid content of the soil, the lower the fixing capacity, and the higher the colloid content, the higher the fixing capacity. However, there are some exceptions—samples 39 and 40 are Hawaiian lateritic soils containing 90 per cent or more of colloidal material, yet they fix no potash. Other exceptions can be found by examining table 2. Thus it is evident that the quality of the colloid of a soil, as well as the quantity, is important in determining its fixing capacity for potassium

Effect of continued potash fertilization on the residual capacity of a soil to fix potash

Two samples of Hagerstown silt loam were obtained, one of which had received no potash fertilizer, and the other, 5,000 pounds of potassium chloride

TABLE 3

Amounts of potash fixed by 100 different soils after potash was added at the rate of 1,000 pounds per acre and then alternately wetted and dried 10 times at 70°C.

NO.	SOURCE OF SAMPLE	TYPE OR KIND OF SOIL	DEPTH OF SAMPLE	AMOUNTS OF POTASH FIXED BY THE SOILS		
				Pounds per acre		Per cent of addition, average
				a	b	
39	Hawaii	Laterite No. 5	Surface	0	0	0
40	Hawaii	Laterite No. 10	Surface	0	0	0
20	Columbia Co., Wis.	Dunning F. S. L.	Surface	0	0	0
22	Washburn Co., Wis.	Vilas sand	Surface	0	0	0
24	Sauk Co., Wis.	Plainfield F. S.	Surface	0	0	0
25	Washburn Co., Wis.	Plainfield sand	Surface	0	0	0
32	Cape Girardeau, Mo.	Kaolin	.....	0	0	0
47	Sparta, Wis.	Plainfield sand	Surface	0	0	0
48	Hancock, Wis.	Plainfield sand	Surface	0	0	0
78	Fresno Co., Calif.	Fresno sand	Surface	0	0	0
69	Montgomery Co., Kas.	Crawford loam	Surface	0	0	0
70	Montgomery Co., Kas.	Crawford loam	Subsoil	809	809	81*
13	Iowa Co., Wis.	Dodgeville Si. L.	Surface	33	23	3
23	Ashland Co., Wis.	Vilas sand	Surface	50	30	4
17	Ashland Co., Wis.	Mellen loam	Surface	60	65	6
26	Waushara Co., Wis.	Coloma sand	Surface	76	...	8
79	New Iberia, La.	Peat	Surface	100	100	10
43	Wisconsin	Knox Si. L.	Surface	121	81	10
27	Columbia Co., Wis.	Coloma sand	Surface	119	...	12
11	Iowa Co., Wis.	Knox Si. L.	Surface	125	125	13
12	Iowa Co., Wis.	Knox Si. L.	Subsoil	338	338	34*
7	Dane Co., Wis.	Miami Si. L.	Surface	131	140	14
8	Dane Co., Wis.	Miami Si. L.	Subsoil	848	848	85*
19	Columbia Co., Wis.	Miami F. S. L.	Surface	144	144	14
46	Marshfield, Wis.	Colby Si. L.	Surface	118	183	15
67	New Iberia, La.	Oliver loam	Surface	142	172	16
68	New Iberia, La.	Oliver loam	Subsoil	186	216	20*
45	Wisconsin	Carrington Si. L.	Surface	163	163	16
28	Dane Co., Wis.	Peat	Surface	146	180	16
73	California	Hanford F. S. L.	Surface	173	173	17
76	California	San Joaquin loam	Surface	190	180	18
18	Douglas Co., Wis.	Mellen loam	Surface	185	195	19
58	California	Imperial clay	Surface	230	180	20
41	Hawaii	Laterite No. 9	Surface	205	215	21
65	New York State	Dutchess stony Si. L.	Surface	229	209	22
38	Ashland, Wis.	Superior clay	Surface	250	205	23
30	Penn. Potash Plat†	Hagerstown Si. L.	Surface	255	230	24

* Subsoil sample corresponding to the surface sample reported immediately below in the table.

† The plat from which this sample was taken received 5,000 pounds of potash over a period of 50 years.

TABLE 3—*Continued*

NO.	SOURCE OF SAMPLE	TYPE OR KIND OF SOIL	DEPTH OF SAMPLE	AMOUNTS OF POTASH FIXED BY THE SOILS		
				Pounds per acre		Per cent of addition, average
				a	b	
37	Wisconsin	Boone S. L.	Surface	273	251	26
63	New Iberia, La.	Iberia Si. L.	Surface	272	262	27
64	New Iberia, La.	Iberia Si. L.	Subsoil	536	536	54*
44	Wisconsin	Carrington Si. L.	Surface	261	282	27
61	Montgomery Co., Kas.	Oswego Si. L.	Surface	305	305	30
9	Fond du Lac Co., Wis.	Fox Si. L.	Surface	308	308	31
10	Fond du Lac Co., Wis.	Fox Si. L.	Subsoil	392	338	36*
14	Dane Co., Wis.	Clyde Si. L.	Surface	285	350	32
3	Fond du Lac Co., Wis.	Superior clay	Surface	315	328	32
4	Fond du Lac Co., Wis.	Superior clay	Subsoil	696	686	69*
54	California	Merced clay adobe	Surface	285	390	34
96	Honduras, C. A.	Alluvial lowland	Surface	333	358	35
21	Waushara Co., Wis.	Coloma S. L.	Surface	360	350	35
50	Wisconsin	Dodgeville Si. L.	Surface	370	370	37
77	California	San Joaquin S. L.	Surface	370	370	37
81	Honduras, C. A.	Alluvial lowland	Surface	382	390	39
74	Calhoune, La.	Orangeburg S. L.	Surface	401	401	40
75	Calhoune, La.	Orangeburg S. L.	Subsoil	392	382	39*
42	Wisconsin	Knox Si. L.	Surface	410	...	41
29	Penn. Check Plat	Hagerstown Si. L.	Surface	405	425	41
99	Honduras, C. A.	Alluvial lowland	Surface	425	415	42
57	California	Porterville clay adobe	Surface	365	495	43
95	Honduras, C. A.	Alluvial lowland	Surface	435	455	44
31	Dane Co., Wis.	Miami Si. L.	Surface	444	454	45
49	Wisconsin	Dodgeville Si. L.	Surface	483	503	49
51	Wisconsin	Waukesha Si. L.	Surface	525	555	54
71	New Iberia, La.	Miller loam	Surface	543	543	54
72	New Iberia, La.	Miller loam	Subsoil	785	765	77*
52	Atlanta, Ga.	Weathered Gneiss	Surface	559	537	55
53	Atlanta, Ga.	Weathered Gneiss	Subsoil	116	116	12*
15	Fond du Lac Co., Wis.	Clyde C. L.	Surface	566	534	55
16	Fond du Lac Co., Wis.	Clyde C. L.	Subsoil	850	893	87*
90	Honduras, C. A.	Alluvial lowland	Surface	565	585	57
62	Baton Rouge, La.	Memphis Si. L.	Surface	588	588	59
80	Honduras, C. A.	Alluvial lowland	Surface	600	580	59
1	Ashland Co., Wis.	Superior clay	Surface	603	603	60
2	Ashland Co., Wis.	Superior clay	Subsoil	763	785	77*
94	Honduras, C. A.	Alluvial lowland	Surface	605	620	61
82	Honduras, C. A.	Alluvial lowland	Surface	645	605	62
5	Fond du Lac Co., Wis.	Poygan clay	Surface	665	643	65
6	Fond du Lac Co., Wis.	Poygan clay	Subsoil	719	708	71*
55	New Iberia, La.	Oliver clay	Surface	675	635	65
56	New Iberia, La.	Oliver clay	Subsoil	415	425	42*
66	New Iberia, La.	Iberia C. L.	Surface	688	688	69

TABLE 3—*Concluded*

NO.	SOURCE OF SAMPLE	TYPE OR KIND OF SOIL	DEPTH OF SAMPLE	AMOUNTS OF POTASH FIXED BY THE SOILS		
				Pounds per acre		Per cent of addition, average
				a	b	
77	Honduras, C. A.	Alluvial lowland	Surface	750	780	76
100	Honduras, C. A.	Alluvial lowland	Surface	807	810	81
91	Honduras, C. A.	Alluvial lowland	Surface	818	808	81
93	Honduras, C. A.	Alluvial lowland	Surface	806	828	82
59	Montgomery Co., Kas.	Summit Si. C. L.	Surface	840	830	83
60	Montgomery Co., Kas.	Summit Si. C. L.	Subsoil	700	700	70*
89	Honduras, C. A.	Alluvial lowland	Surface	841	884	86
98	Honduras, C. A.	Alluvial lowland	Surface	862	873	87
87	Honduras, C. A.	Alluvial lowland	Surface	1,033	1,010	102
84	Honduras, C. A.	Alluvial lowland	Surface	1,033	1,033	103
92	Honduras, C. A.	Alluvial lowland	Surface	1,057	1,024	104
86	Honduras, C. A.	Alluvial lowland	Surface	1,061	1,061	106
88	Honduras, C. A.	Alluvial lowland	Surface	1,093	1,083	108
83	Honduras, C. A.	Alluvial lowland	Surface	1,088	1,088	109
85	Honduras, C. A.	Alluvial lowland	Surface	1,122	1,154	114

over a period of 50 years. Both samples were treated for their capacity to fix potash, and the results are given in table 4. It will be noted that the soil which had received the potash fertilizer in the field fixed only about half as much potash as the unfertilized soil. This would lead one to believe that this soil had fixed a considerable portion of the potash applied, and thus a portion of its fixing material had become saturated.

Effect of lime on fixation

A few isolated tests indicated that liming may be a factor in potash fixation. To ascertain more definitely its effect, experiments were conducted on samples of several soils which were given three distinct treatments; viz., (*a*) one portion of each soil was alternately wetted and dried 10 times at 70°C. (*b*) a second portion was treated with 1,000 pounds per acre of potash as the chloride and then alternately wetted and dried 10 times at 70°C. and (*c*) a third portion was treated with 3 tons per acre of calcium hydroxide as lime water, 1,000 pounds per acre of potash as the chloride, and then alternately wetted and dried 10 times at 70°C. All portions of the soils were then dispersed in normal ammonium acetate, thrown on a filter, and leached practically free of all replaceable and soluble potash. The potash in the leachate was determined in the usual manner.

The results given in table 5 show quite conclusively that lime additions do cause increased potash fixation in soils. The reason for this increase has not been ascertained as yet, but it may be due to the fact that the alkaline condi-

tion produced by the lime hydroxide brings alumina and silica into solution, which, in turn, combine with the potash to form an insoluble potassium aluminum silicate. This increased fixation, caused by lime additions, may explain in part the results obtained by Bledsoe (2), Goethe (8), McCall (16), Plummer (23), and others, who found that calcium carbonate additions in some way limit the amount of potash which the plant is able to take up. Also, it would explain the fact that Lyon and Bizzell (14, 15), MacIntire et al. (18, 19, 20), McCool (17), and Spurway (24) found that calcium carbonate additions do not increase the potash content of drainage water.

Potash fixation by soil minerals

To find out whether a definite mineral in the soil causes the fixation of potash, a series of minerals were finely ground, treated with potassium chloride, and alternately wetted and dried 10 times at 70°C. The results indicated that biotite, nephelite, syenite, anorthite, apophyllite, anorthoclase, chlorite, and

TABLE 4

Effect of 50 years of potash fertilization on Hagerstown silt loam, Pennsylvania station plats, on the potash fixing power of the soil

PLAT TREATMENT IN FIELD	AMOUNTS OF POTASH PER ACRE FIXED FROM A 1,000-POUND LABORATORY APPLICATION		
	Pounds per acre		Per cent of addition
	Test 1	Test 2	
No potash	405	425	41
5,000 pounds of potash added over a 50-year period	255	230	24

talc do not fix potash; but that albite, halloysite, deweylite, and decomposed granite do fix small quantities, though not enough to account for the large fixation in soils.

Minerals isolated by specific gravity methods (29) from soil possessing a fairly high fixing power were treated with 10 tons per acre of potash as the bicarbonate, and were alternately wetted and dried 10 times at 70°C. to induce fixation. Only that portion of the soil having particles >0.002 mm. in diameter was separated into its mineral constituents. The remainder of the soil, the colloidal fraction, was tested as a unit for fixation. The results given in table 6 indicate that very little fixation took place in any of the soil minerals of a diameter greater than 0.002 mm. except for the fraction lighter than specific gravity 2.500, which contained a large amount of undispersed aggregates of colloidal matter. On the other hand, the colloidal fraction of this soil (diameter <0.002 mm.) showed an increase of .60 per cent in total potash content, due to fixation. Thus, it is evident that one should study the colloidal fraction of a soil if one wishes to investigate the constituents causing potash fixation.

TABLE 5

Amounts of potash fixed by limed and unlimed soils

Soils were treated with 1,000 pounds per acre of potash as the chloride and wetted and dried 10 times at 70°C.

SOIL CLASSIFICATION	POUNDS OF POTASH FIXED PER ACRE		
	Unlimed	Limed with 3 tons per acre of calcium hydroxide	Increase due to lime
Hagerstown silt loam	410	488	78
Laterite No. 9	210	287	77
Dodgeville silt loam	370	422	52
Carrington silt loam	270	353	83
Knox silt loam	410	442	32
Waukesha silt loam	540	559	19
Colby silt loam	150	150	0
Superior clay	600	664	64
Carrington silt loam	160	228	68
Miami silt loam	450	450	0
Knox silt loam	100	100	0

TABLE 6

Amounts of potash fixed by minerals from Hagerstown silt loam (Pennsylvania station), when treated at the rate of 10 tons per acre of potash as the bicarbonate, and then wetted and dried 10 times at 60°C.

DIAMETER OF THE MINERAL PARTICLES	SPECIFIC GRAVITY RANGE OF THE MINERAL FRACTIONS	IMPORTANT MINERALS FOUND IN EACH SPECIFIC GRAVITY RANGE OR FRACTION	AMOUNT OF EACH FRACTION CONTAINED IN ONE ACRE OF SOIL	TOTAL NON-REPLACEABLE POTASH IN EACH FRACTION		POTASH FIXATION DURING TREATMENT	
				Before treatment with potassium bicarbonate	After treatment with potassium bicarbonate	As percentage of original total	In pounds per acre
mm.			*pounds*	*per cent*	*per cent*		
>0.002	>2.750	Mica plus heavy iron minerals	36,501	1.20	1.34	11.7	44
	<2.750 >2.655	Plagioclase, mica, and some quartz	36,249	1.50	1.54	2.8	14
	<2.655 >2.620	Mainly quartz	664,091	0.78	0.78	0.0	0
	<2.620 >2.600	Mainly quartz and feldspars	315,733	2.00	2.05	2.5	158
	<2.600 >2.500	Mainly feldspars	270,300	7.98	8.08	1.3	270
	<2.500	Feldspars plus a large amount of low specific gravity minerals	38,674	1.98	2.39	20.7	158
<0.002 (Colloid)	Not determined	No specific gravity separations made	461,797	1.88	3.01	60.1	5,218

Influence of leaching soils with HCl and Na_2CO_3 solutions on potash fixation

It was thought that if one leached a soil with HCl or Na_2CO_3 solutions one might be able to destroy its fixing capacity by removing the fixing material. Two soils were selected, Miami silt loam and Hagerstown silt loam. Twenty-five-gram samples of each were leached 132 hours with *N* HCl, 5,500 cc. being used. Also, a 25-gm. sample of each was leached with *N* Na_2CO_3 for 240 hours, using 5,000 cc. of solution. The leachates were analyzed for alumina and silica, and the leached soils, after being thoroughly washed with water, were tested for fixation of potash. The results, given in table 7, show that the HCl leaching decreased the fixing capacity, whereas the Na_2CO_3 treatment increased it. The analyses of the leachates indicate that aluminum may be in some manner tied up with the fixation of potash. In the case of the HCl treatment, a large amount of Al_2O_3 was removed, and fixation dropped; where-

TABLE 7

Influence of removal of Al_2O_3 and SiO_2 from soils by leaching with N Na_2CO_3 and N HCl on potash fixation

CLASS OF SOIL	PERCENTAGE OF APPLIED POTASH FIXED BY SOILS INDICATED			AMOUNTS REMOVED FROM 25-GM. SAMPLES		
	Normal field soil	Soil leached with *N* HCl	Soil leached with *N* Na_2CO_3	By HCl leaching	By Na_2CO_3 leaching	
				Al_2O_3	SiO_2	Al_2O_3
				gm.	*gm.*	*gm.*
Miami silt loam	45	21	56	1.639	0.125	0.339
Hagerstown silt loam	41	28	75	1.531	0.237	0.177

as in the case of the Na_2CO_3 treatment, only about one-fifth as much Al_2O_3 was removed, and the fixation was increased, a condition which could be explained on the assumption that the Na_2CO_3 formed sodium aluminate, which was retained in the soil and aided potash fixation.

Fixation of potash by synthetic mixtures of sand, silica gel, alumina gel, and calcium hydroxide

To test further the possibility of potash being fixed by its mutual action with silica gel and alumina gel, a series of tests was conducted as tabulated in table 8. Various proportions of silica gel, alumina gel, calcium hydroxide, potassium chloride, and pure sand were mixed together. These mixtures were then wetted and dried alternately 10 times at 70°C. to induce fixation. However, no fixation took place, even under alkaline conditions, since all the potash added was removed by extraction with normal ammonium acetate.

Before further studies were undertaken in an attempt to determine the compounds in the soil responsible for potash fixation, an attempt was made to isolate the compound formed during potash fixation.

Form of potash fixation in Hagerstown silt loam

From the results reported thus far, it is evident that a portion of the soluble potassium added to a soil becomes fixed in a difficultly available form. Evidence also points to the fact that it is not held mechanically. Thus, it seems probable that it is fixed in the form of a new secondary mineral of extremely low solubility. In order to isolate this new mineral, a sample of soil was needed which had been treated for a number of years with potassium salts. For this purpose, samples of Hagerstown silt loam were obtained from plats 1 and 4 of the Pennsylvania station[3] soil fertility field started 50 years ago. Plat 1 is a check and plat 4 has received 200 pounds per acre of potassium chloride biennially since 1881, making 3,158 pounds of potash in all. Approximately 600

TABLE 8

Fixation of potash by various synthetic mixtures. All mixtures were wetted and then dried at 70°C., 10 times

TEST NUMBER	COMPOSITION OF EACH TEST MIXTURE					pH OF THE TEST MIXTURE AT THE END OF THE WETTING AND DRYING PERIOD	EXTENT OF POTASH FIXATION
	Medium white sand	H_2SiO_3 gel	$Al(OH)_3$ gel	$Ca(OH)_2$	KCl		
	gm.	*gm.*	*gm.*	*gm.*	*gm.*		
1	10	0.5	.....	.....	0.008	4.0	None
2	10	0.5	.....	0.25	0.008	8.5	None
3	10	.....	0.5	.....	0.008	8.5	None
4	10	.....	0.5	0.25	0.008	8.5	None
5	10	0.25	0.25	.....	0.008	6.0	None
6	10	0.25	0.25	0.25	0.008	8.5	None

pounds of potash have been removed from the potassium chloride plat in excess of that removed from the check plat by the crops corn, oats, wheat, and hay (7). Also, the sample of soil from the potassium chloride plat contains an excess over the check plat of 336 pounds of available potash. This leaves 2,222 pounds of potash unaccounted for, the greater portion of which is probably fixed in the soil, since potash leaches but little (13).

Preliminary attempts at separating the soil minerals by specific gravity methods led to many difficulties, and methods of separation had to be developed to fit the needs. These methods have been reported elsewhere in detail (29).

Using the methods described elsewhere (29, 30, 31), mechanical, mineralogical, and chemical analyses were made of the Hagerstown silt loam of check plat 1 and potassium chloride plat 4. As shown in table 9, the potassium chloride plat contains 9,266 pounds of total potash in excess of that contained

[3] The writer is greatly indebted to the officials of the Pennsylvania Agricultural Experiment Station for having furnished the samples of Hagerstown silt loam used in this investigation.

TABLE 9

Amounts of minerals and total potash in the soil separates and fractions thereof of the treated and untreated plats of Hagerstown silt loam, Pennsylvania station, the potassium chloride plat having received the equivalent of 3,158 pounds of potash over a period of 50 years, and the check plat having received none

PART OF SAMPLE	SPECIFIC GRAVITY RANGE OF EACH FRACTION PRESENT	MAIN MINERALS PRESENT IN EACH FRACTION	POUNDS OF SEPARATES AND MINERALS IN AN ACRE OF SOIL		PERCENTAGE TOTAL POTASH IN EACH SEPARATE OR FRACTION		POUNDS OF POTASH PER ACRE IN THE SEPARATES AND FRACTIONS		POUNDS PER ACRE OF EXCESS POTASH IN KCl PLAT OVER THAT IN THE CHECK PLAT
			KCl Plat	Check Plat	KCl Plat	Check Plat	KCl Plat	Check Plat	
Entire sample	Not determined	Not determined	1,873,385	1,893,401	2.90	2.38	54,328	45,062	+9,266
Coarse and separate	Not determined	Not determined	52,455	70,056	0.62	0.72	325	504	−179
40 mesh to 0.002 mm. separate	>2.750	Mica plus heavy iron minerals	32,420	36,501	1.28	1.20	415	439	−24
	<2.750 >2.655	Plagioclase, mica and some quartz	28,440	36,249	1.61	1.50	458	544	−86
	<2.655 >2.620	Nearly pure quartz plus some feldspar	614,531	664,091	0.79	0.79	4,854	5,246	−392
	<2.620 >2.600	Mixtures of feldspar and quartz	222,392	315,733	2.11	1.99	4,692	6,283	−1,591
	<2.600 >2.500	Nearly all feldspar	366,279	270,300	8.11	7.99	29,705	21,597	+8,108
	<2.500	Some feldspar plus the light minerals	84,746	38,674	2.04	1.98	1,729	766	+963
<0.002 mm. separate	Not determined	Mainly hydrated secondary minerals	472,122	461,797	2.46	1.88	11,614	8,682	+2,932
Sum of separates			1,873,385	1,893,401	....	....	53,792	44,061	+9,731

in the check plat, but only 2,558 pounds of this amount could have come from the potash added as fertilizer. Since the potassium chloride plat contains considerably more feldspar than the check plat, it is believed that this excess potassium exists as native feldspar. Undoubtedly this difference in the amount of feldspar existed at the time the plats were laid out.

The tests previously discussed in this paper show that potassium fixation occurs almost entirely in the colloidal fraction of the soil. In the colloidal separate (<0.002 mm. diameter), table 9, the total potash content is 2.46 per cent for the potassium chloride plat, and 1.88 per cent for the check plat, or an increase of 0.58 per cent in the potassium chloride plat. Thus, it was

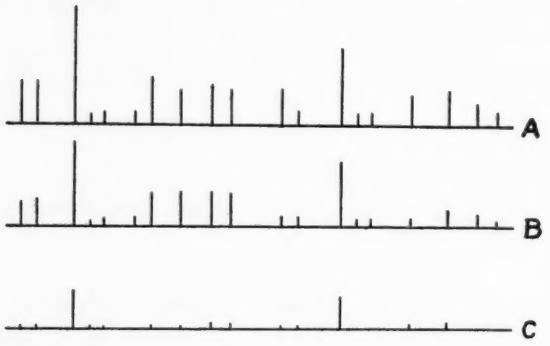

FIG. 4. A COMPARISON OF THE X-RAY PATTERN OF PURE MUSCOVITE WITH THE PATTERNS OF THE HEAVY COLLOIDAL FRACTIONS OF THE POTASSIUM CHLORIDE AND CHECK PLATS OF HAGERSTOWN SILT LOAM, SHOWING MUSCOVITE TO BE MORE PLENTIFUL IN THE POTASSIUM CHLORIDE PLAT

A—Pure muscovite.

B—Potassium chloride plat. Diameter of particles 0.002 to 0.0003 mm. Specific gravity of particles 2.667.

C—Check plat. Diameter of particles 0.002 to 0.0003 mm. Specific gravity of particles 2.667.

decided to study the colloidal fractions of these soils further. Since particles below 0.0003 mm. in diameter could not be separated into mineral fractions by specific gravity means, a separate consisting of particles 0.002 to 0.0003 mm. in diameter was mechanically isolated and separated at specific gravity 2.667. In this manner, all the silica, feldspar, and lighter minerals were separated from the heavier ones. Since petrographic methods (6, 32) could not be applied to these fine fractions as a means of identifying the minerals present, X-ray patterns were obtained for this purpose. The lighter mineral fractions showed only quartz lines, whereas the heavier fractions showed muscovite lines. In the case of the potassium chloride plat, the muscovite lines extended through the second order quite completely, whereas in the case of the check plat they extended into the second order only faintly and incompletely (fig. 4).

This is an indication of the relative amounts of muscovite in the two samples, since their X-ray analyses were made simultaneously.

Chemical analyses were also made of these mineral fractions, as given in table 10. Since the potash content of the coarse portion of the colloid separate (<0.002 and >0.0003 mm. in diameter) is nearly identical with that of the entire colloid separate (<0.002 mm. in diameter), one may assume that

TABLE 10

Minerals in coarse colloid separate as revealed by specific gravity and X-ray analyses, and amounts of these minerals and potash in the entire colloid separate of the Hagerstown silt loam, Pennsylvania station

PLAT SAMPLED	COARSE COLLOID SEPARATE <0.002 AND >0.0003 MM. IN DIAMETER				AMOUNTS IN ENTIRE COLLOID SEPARATE <0.002 MM. IN DIAMETER CALCULATED ON BASIS CONTENT OF COARSE COLLOID SEPARATE		
	Specific gravity of mineral fractions	Percentage total potash in the mineral fractions	X-ray analysis		Pounds per acre of mineral fractions	Pounds per acre of potash in mineral fractions	Pounds per acre excess potash in KCl plat over that in check plat in the mineral fractions
			Minerals shown by X-ray analysis	Remarks			
Check plat received no KCl. .	<2.667	1.74	Quartz	No muscovite lines visible	428,086	7,449	.....
	>2.667	3.90	Muscovite	Muscovite lines extended only through first order	33,711	1,315	.....
KCl plat received equivalent of 3158 pounds per acre of potash	<2.667	2.05	Quartz	No muscovite lines visible	398,671	8,173	724
	>2.667	4.67	Muscovite	Muscovite lines extended through second order	73,451	3,430	2,115

their mineral fractions, as regards potash, are probably similar. Calculated on this basis, the heavy mineral fraction of the entire colloid separate of the potassium chloride plat contains 2,115 pounds of potash in excess of that contained in a similar fraction of the check plat. This is a quantity that almost exactly accounts for the 2,222 pounds of potash added as a fertilizer that could not be accounted for in the sum of the potassium removed by plants and that remaining in the soil in available form. This 2,115 pounds of excess potash is much more than the entire amount found in the corresponding heavy mineral fraction of the check plat, and hence it could hardly be argued that this came largely from the approximately one-fifth more feldspar potash

that exists in the potassium chloride plat over that in the check plat, because that would lead to the implication that more potash came from this one-fifth portion of feldspar than from five times as much feldspar in the case of the check plat.

Thus the conclusion which seems inevitable is that when potassium is added to a soil containing the usual kind of colloidal matter, a portion of it is converted into muscovite, and this potassium is no longer readily available to plants.

Theories regarding the formation of muscovite in the soil

That muscovite is formed in clays, shales, and slates as a secondary mineral, was first suggested by Hutchings (10, 11, 12) in 1890. He states:

> And it is quite reasonable to suppose that when kaolin is deposited together with much feldspar, biotite, muscovite, etc., the changes which afterwards take place, involving as they do a micaceous alteration of the feldspar with liberation of alkaline silicate in solution, may effect a conversion of more or less of the kaolin into mica, a process chemically quite simple, and quite probable under the conditions of pressure and temperature we know to have existed.

Since it has been noted that heavy lime additions to soils may cause a decrease in avilable potassium, probably through fixation, another explanation can be offered for the formation of the muscovite in soils. By the addition of lime, potassium carbonate is forced into solution, and reaches a considerable concentration as the soil dries. This alkali carbonate attacks colloidal silica, colloidal alumina, and colloidal silicates in general, with the ultimate result that muscovite is formed either directly or through the reaction of the intermediate compounds. It should, however, be noted that, since fixation takes place when KCl is added to acid soils, alkalinity does not appear to be a necessary condition for fixation. The influence of lime and sodium carbonate could be explained as being due to the fact that they tend to keep the potassium out of the exchange material and hence in active condition to react with some form of colloidal silicate so as to form muscovite.

Other theories could be proposed, but the findings to date do not seem to warrant further speculation.

Practical applications of the results reported herein

Very likely there have been instances where the application of potash fertilizers has not given full crop response because of the high fixing capacity of the soil for potash.

From the standpoint of applying potash fertilizers under field conditions so as to reduce to a minimum the amount of potash that would be lost by fixation in difficultly available form, three practices are suggested: (*a*) frequent moderate applications instead of less frequent large applications of potash fertilizer, (*b*) application of the fertilizer to a greater depth than usually practiced, so as to get below the surface zone, which is subjected to frequent wetting and

drying, and (*c*) localized application of the fertilizer in the hill or row as to reduce the opportunity for fixation.

It should be noted in this connection that occasional burning and drying of a soil increases the immediate supply of readily available plant nutrients, including potash, as a result of their liberation from organic and possibly certain inorganic constituents. The processes involved are quite different from those discussed in this paper; for a detailed discussion and extensive review of the literature regarding this phase of the subject the reader is referred to the papers of Steenkamp (25, 26, 27).

SUMMARY

The purpose of this investigation was to study the nature of potash fixation, and to determine, if possible, the identity of the difficultly available compound formed when soluble potassium salts are added to soils. Samples of soils were treated with varying quantities of potassium bicarbonate or potassium chloride, moistened with water, and either allowed to dry slowly at room temperature or were alternately wetted and dried a number of times at 70°C. In order to determine the identity of the difficultly soluble mineral formed, a mechanical, mineralogical, chemical, and X-ray study was made of a sample of Hagerstown silt loam which had received a total of 5,000 pounds per acre of potassium chloride during the past 50 years, about half of which could not be accounted for in the potassium removed by the plants and remaining in the soil in available form. The results of the investigation are as follows:

Alternate wetting and drying of soils treated with soluble potassium salts caused rapid fixation of the potassium in a non-replaceable form. When these soils were kept continuously moist, very little fixation of this kind took place.

Ten alternate wettings and dryings usually sufficed to cause a maximum amount of fixation.

In four soils investigated, the ultra clay fraction contained the lowest percentage of total potash of any of the fractions, but, on the other hand, was by far the most active in fixation.

One hundred soils, treated with 1,000 pounds of potash per acre, showed a capacity to fix potash from nothing to all that was added.

Fixation is dependent on the nature of the colloids as well as the quantity. A lateritic soil, containing around 90 per cent colloid, did not fix potash, whereas Miami silt loam, containing only 24 per cent of colloid, fixed 495 pounds per acre out of 1,000 pounds added.

Potash fixation was reduced by leaching soils with HCl, and increased by leaching them with Na_2CO_3.

Most soils, alternately wetted and dried after treatment with 3 tons of calcium hydroxide per acre, were found to fix more potassium than those not treated with calcium hydroxide.

Synthetic mixtures of alumina gel, silica gel, calcium hydroxide, and sand did not fix potash.

Mineralogical, chemical, and X-ray analyses of Hagerstown silt loam from the Pennsylvania station experimental plats, some of which had received 5,000 pounds per acre of potassium chloride over a period of 50 years, led to the conclusion that a portion of the added potassium had reacted with colloidal silicates and become fixed in the form of muscovite, thus converting added available potassium into difficultly available form.

From a practical standpoint it would seem to be advisable to make frequent moderate applications of potash fertilizer rather than less frequent large applications, and also to apply the potash to a greater depth than is usually practiced, in order to lessen the influence of alternate wetting and drying. Localized application would also tend to reduce fixation.

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THE DISTINCTION BETWEEN MAGNESIUM ABSORBED AND THAT EXCHANGEABLE, FOUR YEARS AFTER LYSIMETER INCORPORATIONS OF OXIDES AND CARBONATES

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In certain cylinder experiments, begun in 1913, it was found that the fate of heavy incorporations of hydroxy magnesium carbonate differs from that of equivalent incorporations of calcium carbonate. The "light" magnesium carbonate was absorbed more rapidly and also more extensively (8). In contrast with the large increases in carbonates found 8 weeks after incorporation of burnt lime, hydrated lime, and calcium carbonate at the rate of 16,000 pounds of CaO per acre, only meager carbonate residues were found for the equivalent incorporations of hydroxy magnesium carbonate. Subsequent to the early absorption of the magnesium carbonate, with and without manure, a marked temporary toxicity developed (9). In later supplemental studies, with tobacco, it was determined that additions of caustic magnesia reacted extensively with silicic acid (6).

Since the heavy additions of magnesium carbonate used in the cylinder experiments had been quickly and completely absorbed by the slightly acid and well-buffered Cumberland loam, the study was continued and amplified to determine the ultimate absorption-capacity of that soil. For this purpose a 44-unit lysimeter installation was provided to compare the absorptions from seven calcic and magnesic materials at the CaO-equivalent rates of 8, 32, and 100 tons so that ultimately a balance could be struck between the amounts added, those leached, and those residual in the carbonate and non-carbonate forms. During the first year of this supplemental lysimeter study it was again found that the absorption of the magnesium carbonate was more rapid and more extensive than that of calcium carbonate.

When the lysimeter experiment was inaugurated, the crystalline normal carbonate could not be obtained, and it was known that the precipitated carbonates used in the cylinder and lysimeter studies were combinations of $MgCO_3$ and $Mg(OH)_2$. It was assumed, however, that the CO_2-enriched atmosphere and the carbonated free water of the soil would gradually convert the $Mg(OH)_2$ contents of the hydroxy carbonates into $MgCO_3$ and that the unabsorbed fractions of the additions would ultimately be present as the normal carbonate. From attempts to determine their fate at intervals during a 12-year period, it appeared that the unabsorbed fractions of the heavier additions of the hydrated carbonate continued as such. This was true, in spite

of the fact that large quantities of magnesium bicarbonate had passed out in the leachings. It therefore seemed necessary to provide substantial quantities of the magnesia-treated soils for laboratory study. Samples of such proportions could not be removed from the lysimeters of the long-period experiment without involving correction-computations and vitiating disruptions, especially in the case of the subsoil tanks. The initial lysimeter installation was therefore supplemented by additional tanks, the entire contents of which were to be available for laboratory study after an appropriate period of exposure, and the soils of this supplemental set of lysimeters were used in the present study.

EXPERIMENTAL

Objectives. This 9-unit adjunct lysimeter project was inaugurated in July 1925, to run for a period of 4 years. The outgo data have been reported (7). The present contribution deals with the influence of form and rate of magnesic treatments upon (*a*) extent of absorption, (*b*) nature of the absorbed magnesia as reflected by its exchangeability and solubility in dilute acids, (*c*) the ions replaced by the absorbed magnesium, and (*d*) any corollary chemical effects.

Soil and treatments. The soil was the same Cumberland loam used in the previous cylinder and lysimeter experiments. The five magnesic materials, "light" and "heavy" oxides, "light" and "heavy" hydroxy carbonates, and the crystalline normal carbonate, $MgCO_3 \cdot 3H_2O$ were used. The last-named material had been prepared in the laboratory and identified. It was used because of its high solubility, as compared with the natural carbonate, magnesite. It is not ordinarily listed as a chemical, but it was ultimately obtained in quantities sufficient for the heavy lysimeter treatments. The materials were thoroughly incorporated with the soil before placement in the lysimeters and no subsoil stratum was used. On the basis of CaO equivalence per 2,000,000 pounds of soil, the experimental set-up, with a rainwater blank, was as follows:

Unit 200	Untreated soil
Unit 201	"Light" magnesium oxide, 8 tons
202	"Heavy" magnesium oxide, 8 tons
Unit 203	"Light" precipitated magnesium carbonate, 8 tons
204	"Heavy" precipitated magnesium carbonate, 8 tons
205	Crystalline normal magnesium carbonate, 8 tons
Unit 206	"Light" magnesium oxide, 32 tons
207	"Light" precipitated magnesium carbonate, 32 tons
208	Crystalline normal magnesium carbonate, 32 tons

At the end of the 4-year period of leaching by rainfall only, the soils were removed from the lysimeters and thoroughly mixed, to provide substantial 0.5-mm. samples for the analyses given in tables 1–6. Sufficient opportunity was thus afforded for extensive reaction between the soil and the added magnesic materials and, presumably, for complete carbonation of the magnesium oxide.

Presentation of data. The results are given in terms of milliequivalents of magnesium. The carbonate residues from the five 8-ton oxide and carbonate additions were small and the magnesium increases were therefore practically the same as the respective amounts absorbed, or fixed. The crystalline carbonate unit 205 will therefore be taken to represent the treatments at the 8-ton rate.

To compute the absorptions from the several magnesic materials, it was necessary to determine the final occurrences of both magnesium and carbonate CO_2. In making a comparison between the increases in CO_2 derived from the several additions it was also necessary to assume a common ultimate composition for the residues of magnesium carbonate. Opportunity to differentiate, with some degree of certainty, between the forms that make up the unabsorbed fractions of the added magnesic materials was therefore limited to the 32-ton units, all of which contained substantial carbonate residues.

The leaching data (7) indicated that the heavy outgo of magnesium bicarbonate from the normal carbonate brings about an accumulation of the hydroxy carbonate, as represented by the equation:

$$5MgCO_3 + 2H_2O \rightarrow \underset{\text{accumulated}}{3MgCO_3 \cdot Mg(OH)_2} + \underset{\text{leached}}{MgH_2(CO_3)_2}$$

As previously noted, it also appeared that the incorporations of the hydrated carbonates, represented by the formula $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, had not been converted into the normal carbonate, $MgCO_3 \cdot 3H_2O$. In accounting for the magnesium present in the carbonate form, it therefore seemed logical to assume that the hydrated carbonate would be the one more likely to be present. Under this assumption, the unabsorbed magnesium is $33\frac{1}{3}$ per cent greater than the amount that would be computed from a simple CO_2 equivalence. The CO_2 results from the oxide additions were computed in the same manner, but the relationships in the oxide systems are more involved. It is well known that properties of magnesium oxide are specific for the different types obtained from different carbonates and that calcination temperatures materially affect the reactivities of the calcined product. A part of the unabsorbed fraction of added oxide may continue as such, a part may be present as the hydrated oxide, and the remainder as the carbonate. This point will be considered further in a discussion of the computations for the absorptions.

Extent of magnesia absorptions. The increases in magnesium, as determined by digestion with HCl, sp. gr. 1.115, and the carbonate occurrences, are given in table 1. The fundamental data of this table are used as the basis of comparison for all of the leachate and extraction data presented in tables 2–6. As previously explained, table 1 shows the quantities of "unabsorbed" magnesium present in the postulated form of $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. The values for "absorbed"magnesia are shown in the last column, and are the respective differences between the values for "increase" and "unabsorbed."

It is evident that the absorption from each of the 32-ton treatments greatly

exceeds that found for the 8-ton rate. The maximal absorption capacity of the heavy clay loam for magnesium for the 4-year period of moist contact and dynamic condition was about 2 per cent $CaCO_3$ equivalence, or 20 tons per 2,000,000 pounds of soil. The computation of 3.102 per cent, or 62.04 m.e., for absorption in the oxide unit 206 is obviously in excess of the true value, because from the determined carbonate occurrence of 0.599 per cent it is evident that a considerable part of the added oxide had not been converted to the carbonate. It has been shown (7) that in spite of this incomplete transition of oxide to carbonate, the $CaCO_3$-equivalence of the carbonates leached from the 32-ton addition of magnesic oxide by the rainwater during 4 years far exceeded that leached from the equivalent treatment of hydrated carbonate—12.93 tons against 10.59 tons. Hence, in spite of the fact that the oxide residue from unit 206 was bathed copiously with solutions of magnesium bicarbonate for 4 years, the gain in carbonates was only 30 per cent of the carbonate residue from the equivalent addition of hydroxy carbonate. The carbonate gain for the oxide was only 0.599 per cent against 3.90 per cent for magnesium "increase," whereas the residual carbonate from the hydroxy carbonate of unit 207 was 1.942 per cent along with the total magnesium gain of 4.29 per cent. The ratio between carbonate increase and total magnesium increase was therefore 1:6.5 for the oxide addition, as compared with corresponding ratios of 1:2.16 and 1:3.17 for the equivalent treatments of the hydroxy carbonate and the normal carbonate, respectively.

Although the heavy addition of oxide yielded large quantities of magnesium bicarbonate to the rain water leachings over the 4-year period, as shown previously (7), the air-dried uncarbonated residue was not active toward a moist absolute CO_2 atmosphere. No increase in carbonates was found for the soil of either unit when 15-gm. air-dried charges of the oxide unit 206 and the hydrated carbonate unit 207 were bathed for 72 hours with currents of CO_2 that previously had passed slowly through a column of water in "worm" scrubbers. These two soils were then mixed with pure quartz, and the mixtures were moistened and accorded the same contact with an atmosphere of CO_2 for a 72-hour period. The moist mixture of the oxide unit 206 gained 0.062 per cent CO_2, on the basis of original air-dry soil. That is, after this subsequent carbonation, the carbonate-accumulation value that had been found for the 32-ton oxide unit at the end of 4 years of lysimeter exposure was increased from 0.599 per cent to 0.740 per cent. Hence, on the assumption that the amount of magnesium absorbed from the oxide was the same as that absorbed from the hydroxy carbonate—a liberal assumption—the unabsorbed residue of the oxide addition was 36 per cent uncarbonated. There was no difference, however, between the carbonate content of unit 207 before and after the additional exposure to a moist atmosphere of CO_2. It is therefore evident that the uncarbonated oxide residues continued to show a slow transformation to carbonates, and that the hydrated carbonate was not transformed into the normal carbonate.

TABLE 1

Magnesium residues in a Cumberland clay loam 4 years after incorporations of equivalent additions of oxide and hydroxy and normal carbonates of

TABLE 1

Magnesium residues in a Cumberland clay loam 4 years after incorporations of equivalent additions of oxide and hydroxy and normal carbonates of magnesium in outdoor lysimeters

UNIT	MATERIALS INCORPORATED			MAGNESIUM AS PER CENT $CaCO_3$⇔ AND AS MILLIEQUIVALENTS									
	Form	Amount*		Soluble in 1.115 HCl				Carbonates		Unabsorbed†		Absorbed	
		Per cent $CaCO_3$⇔	m.e.	Found		Increase							
				per cent	*m.e.*	*per cent*	*m.e.*	*per cent*	*m.e.*	*per cent*	*m.e.*	*per cent*	*m.e.*
200	None	.....	.....	0.65	13.00	....	.....	.....	.....	.....	.....	.....	.....
205	Crystalline normal carbonate‡	1.4285	28.57	1.25	25.00	0.60	12.00	0.075	1.50	0.100	2.00	0.500	10.00
206	"Light" oxide	5.7140	114.28	4.55	91.00	3.90	78.00	0.599	11.98§	0.798	15.96§	3.102	62.04§
207	"Light" precipitated carbonate	5.7140	114.28	4.94	98.80	4.29	85.80	1.942	38.84	2.589	51.78	1.701	34.02
208	Crystalline normal carbonate	5.7140	114.28	4.09	81.80	3.44	68.80	1.086	21.72	1.448	28.96	1.992	39.84

* Equivalent to rates of 8 and 32 tons CaO per 2,000,000 pounds of soil.
† Computed from CO_2 data, on the assumption that the unabsorbed fraction of the added magnesium is present as $3\,MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$.
‡ Representative of four other practically completely absorbed additions of "light" and "heavy" oxides and their corresponding carbonates.
§ The value computed for "absorbed" is obviously high and that computed for "unabsorbed" is low because of the incomplete carbonation of the added oxide.

TABLE 2

Magnesium recoveries by normal ammonium chloride leachings *of the residues from equivalent additions of oxide and hydroxy and normal carbonates, 4 years after incorporations in outdoor lysimeters*

UNIT	MATERIALS INCORPORATED			MAGNESIUM EXTRACTED FROM 25-GM. CHARGES BY SUCCESSIVE 500-ML. LEACHATES									
	Form	Amount*		1	2	3	4	5	6	7	8	Total	Recovery
		Per cent $CaCO_3$⇔	m.e.										
				m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*
200	None	.....	.....	1.12	0.62	0.28	0.30	0.14	0.02	0.10	0.06	2.64	....
205	Crystalline normal carbonate†	1.4285	28.57	9.28	1.40	0.82	0.66	0.66	0.14	0.14	0.10	13.20	88.0
206	"Light" oxide	5.7140	114.28	31.36	9.22	5.98	5.56	3.56	2.18	1.88	1.38	61.12	75.0
207	"Light" precipitated carbonate	5.7140	114.28	57.50	6.12	4.06	3.56	2.24	1.38	1.16	0.82	76.84	86.5
208	Crystalline normal carbonate	5.7140	114.28	38.18	6.42	4.52	4.02	2.50	1.46	1.36	0.78	59.24	82.3

* Equivalent to rates of 8 and 32 tons CaO per 2,000,000 pounds of soil.
† Representative of four other practically completely absorbed additions of "light" and "heavy" oxides and the corresponding carbonates.

MAGNESIUM RECOVERIES

Ammonium chloride leachings. The results of table 2 show the recoveries from each of the five units of table 1, by eight successive 500-ml. leachings with a neutralized normal solution of ammonium chloride, according to the Hissink procedure (2). Five leachings were required to reduce the yields from the 8-ton unit 205 to the level found for the control, and to effect a recovery comparable to that shown by the strong acid digestion of the same unit in table 1. In the first leachates, wherein direct solvent action was at play, the recoveries from the two 32-ton carbonate additions were considerably greater than the recovery from the oxide, although the oxide residue exceeded that of the crystalline carbonate. The ultimate recoveries assumed the same order as that of the

TABLE 3

Magnesium recoveries from additions of oxide and hydroxy and normal carbonates made to an air-dry Cumberland clay loam immediately preceding *leaching with normal ammonium chloride*

MAGNESIUM ADDITIONS TO ACID SOIL CONTROL*			MAGNESIUM EXTRACTED FROM 25-GM. CHARGES BY SUCCESSIVE 500-ML. LEACHATES								
Form	Amount		1	2	3	4	5	6	7	8	Total
	Per cent $CaCO_3$ eq.	m.e.									
			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
"Light" oxide	1.398	27.96	27.34	0.76	0.42	0.22	0.16	0.06	0.08	0.08	29.12
Light precipitated carbonate	1.448	28.96	29.42	0.38	0.24	0.26	0.08	0.06	0.26	0.08	30.78
Normal crystalline carbonate	1.658	33.16	34.08	0.48	0.32	0.18	lost	0.04	0.10	0.46	35.66

* Same as unit 200, tables 1, 2, and 6.

total residues. Appreciable quantities of magnesium were recovered from each of the heavy treatments, even in the eighth leachate. Apparently the continued leachate recovery was due to the fact that a large part of the absorbed magnesium was resistant to exchange for the NH_4 ions.

To demonstrate that this extended recovery was not attributable to protracted direct solvent action of the neutralized ammonium chloride solution upon the different unabsorbed residues of the several magnesic additions, the following procedure was carried out. The light oxide, the light hydroxy carbonate, and the normal carbonate were added separately to the air-dried original soil in amounts comparable with the respective quantities of the same three materials that remained after 4 years of exposure to leaching. The several fortified charges of the air-dry control soil were then immediately extracted with a normal solution of ammonium chloride, exactly as in the procedure that had been followed in obtaining the results of table 2. The data of table 3 demonstrate that the laboratory additions were entirely removed

by the first 500-ml. leachates. The subsequent leachates from the fortified charges were at the low levels shown for the untreated soil in table 2. When the totals given in the last column of table 3 are corrected for the magnesium leached from the untreated soil, table 2, the recoveries agree with the laboratory additions made to the air-dried control. When these results are used as criteria for the identical ammonium chloride leachings from the 32-ton lysimeter units, it is concluded that the extended magnesia recoveries of table 2—evidenced even in the eighth 500-ml. leachate—were due to the continued removal of absorbed magnesia from the absorption complex, rather than to meager and extended dissolving of the unabsorbed magnesium residues. It is certain that the exchange between the tenaciously held magnesium and the NH_4 ions of the ammonium chloride solution was not so readily effected as that found for *native* supplies of exchangeable magnesium with limited leachates of 300 to 500 ml., as in the Hissink method (2).

The exchangeability of the absorbed magnesia was determined by the method proposed by Kelley and Brown (3). The amounts of ammonia exchanged and retained by the five soils of tables 1 and 2 during 4-liter leachings with a normal solution of ammonium chloride were:

	CONTROL, NO ADDITION	UNIT 205, 8 TONS NORMAL CARBONATE	UNIT 206, 32 TONS LIGHT OXIDE	UNIT 207, 32 TONS LIGHT PPT. CARBONATE	UNIT 208, 32 TONS NORMAL CARBONATE
m.e.	8.8	9.0	9.0	9.2	9.0

The exchange capacity of the untreated soil was practically the same as that found for the four magnesia-treated lysimeter soils. These uniform ammonium recoveries are only about 55 per cent of the equivalence of the magnesium + calcium removed from the 8-ton unit 205 by the leaching procedure. In a comparison of the varying and extended recoveries of magnesium effected by the ammonium chloride leachings and the exchange capacity results by the Kelley and Brown procedure after the 4-year period of contact, it is evident that the exchange capacities of the several units are not correlated with the magnesium absorptions. Only a small fraction of the large quantities of the absorbed magnesium was in the exchangeable state, in the accepted meaning of the term. Hence, any upbuilding, or enrichment, of magnesium in the exchange complex that may have transpired as a result of the magnesic additions was not registered by either the Hissink procedure or that of Kelley and Brown.

The difference between the magnesium absorption and the ammonium exchanged by the magnesium-enriched soils during the leachings with neutralized solution of ammonium chloride may be attributed, of course, to the influence of pH values. The absorption of NH_4 ions from the solution of ammonium chloride represents the absorption capacity of the soil for a solution having a pH of 7.0, whereas the magnesium absorption in the lysimeter units reflects

the absorption capacity for magnesium at a pH of approximately 9. Another important difference is that of the time of contact.

Ammonium chloride extractions. Since complete recoveries of the absorbed magnesium were not obtained by the leachings with normal solutions of ammonium chloride, the 32-ton units 206, 207, and 208 were subjected to repeated *extractions* with both ammonium chloride and dilute acids, and also to successive leachings with dilute acids, according to the Gedroiz method (1).

The recoveries obtained by successive agitated overnight extractions with a neutralized normal solution of ammonium chloride are given in table 4. The

TABLE 4

Magnesium recoveries by normal ammonium chloride extractions of the residues from equivalent additions of oxide and hydroxy and normal carbonates 4 years after incorporations in outdoor lysimeters

UNIT	MATERIALS INCORPORATED			MAGNESIA RECOVERIES BY SUCCESSIVE 500-ML OVERNIGHT EXTRACTIONS OF 25-GM. CHARGES					
	Form	Amount*		1	2	3	4	Total	Recovery†
		Per cent $CaCO_3$ equiv.	m.e.						
				m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*
200	None	.....	.....	0.54	0.04	0.04	0.04	0.66	..
205	Crystalline normal carbonate‡	1.4285	28.57	8.04	0.74	0.40	0.48	9.66	81
206	"Light" oxide	5.7640	114.28	30.64	10.64	6.28	5.30	52.86	68
207	"Light" precipitated carbonate	5.7140	114.28	52.08	10.88	5.04	4.04	72.04	84
208	Crystalline normal carbonate	5.7140	114.28	36.60	10.24	5.50	4.04	56.38	82

* Equivalent to rates of 8 and 32 tons CaO per 2,000,000 pounds of soil.

† Based on the "increase" values shown in table 1.

‡ Representative of four other almost completely absorbed additions of "light" and "heavy" oxides and the corresponding carbonates.

magnesium removed from the untreated soil by these four extractions was less than the amount removed by the first four of the eight leachates of table 2. The same holds true for the soil of the 8-ton unit 205. The same comparison shows a close agreement for the oxide and hydroxy carbonate units 206 and 207, with a difference of 3.24 m.e. in the case of the normal carbonate unit 208.

The *total* recoveries obtained by the eight leachates were in excess of those obtained by the four extractions in all cases, although the results for the carbonate units 207 and 208 did not vary widely. It is evident that the smaller number of extended agitated extractions were almost as effective as twice the number of leachings, but full recoveries of total residues were not obtained by either of the procedures.

Acid digestion-leachings. In the procedure for acid leaching, following a

digestion period, 25-gm. portions of soil were treated in 250-cc. beakers with an amount of 0.1 *N* HCl just sufficient to decompose the determined amounts of carbonates present. The beakers containing soil and 0.1 *N* acid were placed on a water bath at a temperature of 70°C. for 1 hour and permitted to stand overnight. The acid-digested soils were then filtered and leached as prescribed by Gedroiz, except that 0.02 *N* HCl was used in order to minimize the solubility of manganese and of aluminum. Four successive 500-ml. volumes of leachates were collected, and each leachate was analyzed for both magnesium and calcium. The data of table 5 show that the magnesium recoveries by this acid digestion-leaching treatment were not equal to those obtained by the strong acid digestions of table 1. Nevertheless, the leachings with 2 liters of 0.02 *N* acid gave recoveries materially greater than those obtained by ammonium chloride in the 4-liter leachates shown in the last column of table 2, and by the four successive extractions of table 4.

TABLE 5

Magnesium recoveries by 0.02 N HCl leachings of the residues from equivalent additions of oxide and hydroxy and normal carbonates 4 years after incorporations in outdoor lysimeters*

UNIT	MATERIALS INCORPORATED	MAGNESIUM EXTRACTED FROM 25-GM. CHARGES BY SUCCESSIVE 500 ML. LEACHATES					
		1	2	3	4	Total	Recovery†
		m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*
206	"Light" oxide	30.52	15.32	14.46	11.28	71.58	92
207	"Light" precipitated carbonate	57.98	12.52	8.84	2.40	81.74	95
208	Crystalline normal carbonate	40.60	9.62	9.56	3.58	63.36	92

* Equivalent to 5.714 per cent $CaCO_3$, 114.28 m.e. and rate of 32 tons CaO per 2,000,000 pounds of soil.

† Based on the "increase" values shown in table 1.

Agitated acid extractions. The repeated acid extractions with continuous agitation were carried out as follows: Ten-gram charges of the five units of tables 1, 2, and 4 were subjected to four successive 16-hour, or overnight, agitated extractions in the cold with 0.02 *N* HNO_3. In each of the initial extractions, sufficient 0.05 *N* acid was used to decompose the carbonates and still give a residual strength of 0.02 normality. The agitated suspensions were then thrown on Büchner funnels and washed three times with distilled water, and the soil was returned to the original flask with a measured quantity of 0.02 *N* HNO_3 for each succeeding extraction. The four successive filtrates were made to volume, and aliquots were used for the determinations of the "acid-neutralized" and "magnesia-extracted" results of table 6.

The "recovery" values of table 6 give the respective variations from the "increase" values shown for the strong HCl extractions of table 1. In each instance the full magnesium "increase" obtained by the strong acid was also obtained as "total" by the four extractions with 0.02 *N* acid and even by the

TABLE 6

Acid neutralized by, and magnesium recoveries from, absorbed and unabsorbed residues during four agitated overnight extractions, 4 years after equivalent incorporations of oxide and hydroxy and normal carbonates in outdoor lysimeters

UNIT	MATERIALS INCORPORATED		RESULTS OF SUCCESSIVE 500 ML. EXTRACTIONS OF 10-GM. CHARGES WITH 0.02 NORMAL HNO_3											
	Form	Amount*	Acid neutralized					Magnesium extracted					Magnesium recovery	
			1	2	3	4	Total	1	2	3	4	Total		
		m.e	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*
200	None	.....	5.80	0.40	1.00	1.00	8.20	1.08	0.42	0.24	0.32	2.06	.....	.....
205	Crystalline magnesium carbonate†	28.57	18.60	2.80	0.00	0.20	21.60	12.04	0.94	0.44	0.26	13.68	+1.6	+.08
206	"Light" oxide	114.28	82.20	3.00	1.20	0.00	86.40	76.84	1.74	0.64	0.36	79.58	+1.6	+.08
207	"Light" precipitated carbonate	114.28	87.80	4.20	1.60	1.40	95.00	83.62	2.40	0.82	0.36	87.20	+1.4	+.07
208	Crystalline normal carbonate	114.28	73.40	2.40	1.00	0.00	76.80	68.90	1.76	0.72	0.28	71.66	+2.8	+.14

* Equivalent to rates of 8 and 32 tons CaO per 2,000,000 pounds of soil.

† Representative of four other practically completely absorbed additions of "light" and "heavy" oxides and the corresponding carbonates.

first two extractions with the dilute acid. Allowing for the cumulative analytical error, attributable to incomplete precipitation of calcium, in the eight analysis of solutions rich in magnesium and poor in calcium, the results by the two methods may be considered as being in close agreement. Hence, in these experimental soils, there was no appreciable difference between the solubility found for the absorbed magnesium by strong acid digestion and the aggregate dilute acid-extraction value that is ordinarily designated as "exchangeable," and as determined by the Gedroiz method.

"*Acid neutralized.*" The determinations of the quantities of acid neutralized by the magnesium residues in the several soils of table 6 served to record the progress of the extractions before the extracts could be analyzed and they also served as checks upon the respective sums of the several cations. Each "acid neutralized" value exceeds the corresponding value for magnesium extracted but is within 0.1 per cent of the directly determined corresponding sum of the extracted magnesium and (unreported) calcium.

It has been pointed out that the amount of calcium extracted from each lysimeter unit was greater than that extracted from the untreated soil. This apparent discrepancy is accounted for readily. The calcium content of each treated unit was actually in excess of that of the untreated control soils, and for two reasons. The added magnesic materials exerted a marked repressive effect upon the outgo of calcium during the 4-year period of lysimeter exposure. In terms of $CaCO_3$ the averaged outgo of calcium from the three 32-ton treatments was 1,373 pounds less than the calcium outgo from the untreated soil (7). Furthermore, some calcium was introduced, even by the "c.p." magnesic materials. The calcium impurities in the light oxide, carbonate, and normal carbonate were 3.64, 1.26, and 0.22 per cent, respectively, by the methyl-ethyl alcohol method which was used in making all of the magnesia determinations reported. It should be noted that when small quantities of calcium occur with preponderant quantities of magnesium, calcium cannot be determined by the conventional oxalate method of precipitation (5).

Other changes in solubility. It seemed desirable to determine the effects exerted by the magnesic materials upon the solubility of the soil complexes. The acid extracts of table 6 were therefore analyzed for iron and aluminum. The amounts of aluminum extracted from the soil that received the heavy magnesic treatments were much greater than those extracted from the untreated soil. Increases in extractable aluminum were noted especially in the first two extractions, diminishing in the third extraction, and they were not registered in the fourth extraction. The sesquioxide totals removed by the first three extractions were 0.366 per cent for the untreated soil, and 0.405, 0.557, 0.492, and 0.545 per cent for units 205, 206, 207, and 208, respectively. The proportion of iron to aluminum in the extracts from the untreated soil was decidedly different from that found in the extracts from the magnesia-treated units. The ammoniacal precipitates of the acid extractions from the magnesia-treated units were composed almost entirely of alumina, whereas

those from the untreated soil contained a high proportion of iron. Although it has been shown that additions of caustic magnesia will react with colloidal silica that may be present in the soil (6), the foregoing observations indicate

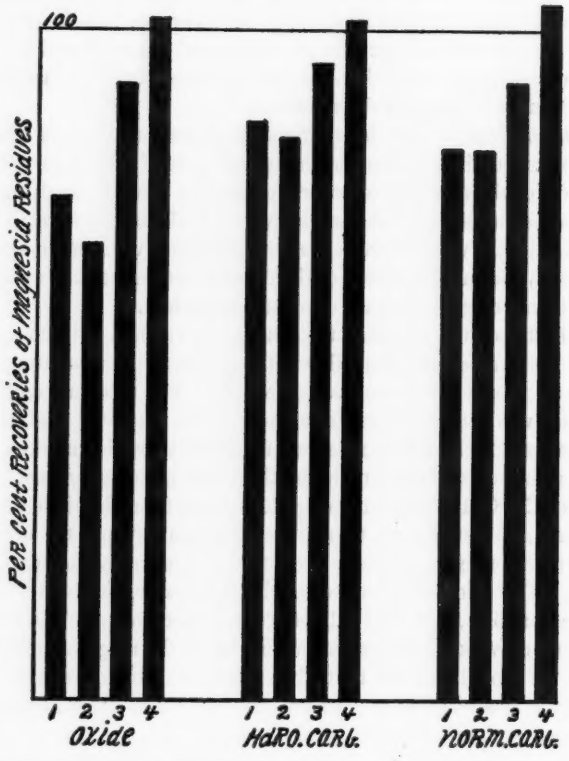

FIG. 1. COMPARISON OF FOUR PROCEDURES IN EFFECTING RECOVERIES OF THE MAGNESIUM RESIDUES FROM 32-TON CaO⇔ ADDITIONS OF OXIDE, HYDROXY CARBONATE, AND NORMAL CARBONATE 4 YEARS AFTER INCORPORATIONS IN OUTDOOR LYSIMETERS

Full "increase" of table 1 used as 100 per cent.

1. Eight 500-ml. *leachings* with *N* NH_4Cl, table 2.
2. Four 500 ml. *extractions* with *N* NH_4Cl, table 4.
3. Four 500-ml. *leachings* with 0.02 *N* HCl, table 5.
4. Four 500-ml. *extractions* with 0.02 *N* HNO_3, table 6.

that the absorbed magnesium had entered into the structure of the aluminum silicate complexes of the soil.

Exchange capacity vs. magnesia absorptions. The total exchange capacity of the Cumberland loam, as determined by the fixation of NH_4 from a neutralized normal solution of ammonium chloride, was 8.8 m.e. This total value

was accounted for by 3.6 m.e. of exchangeable calcium, 1.12 m.e. of exchangeable magnesium, 0.48 m.e. of exchangeable potassium, negligible sodium, and 3.6 m.e. of exchangeable hydrogen, or 41 per cent unsaturation. Since the exchangeable calcium in each of the magnesia-treated lysimeter soils was more than that of the control after 4 years of leaching, because of the marked *decrease in calcium leached* from all of the magnesic treatments (7), and since all of the magnesic treatments also decreased materially the outgo of potassium (7), it is evident that only hydrogen replacement remains to explain a direct chemical absorption of magnesium. But the average absorption of magnesium shown for the two carbonate units 207 and 208 in table 1 was 1.847 per cent (36.94 m.e.) or more than 10 times the amount of exchangeable hydrogen registered by the ammonium chloride methods. All of this absorbed magnesium was recovered by agitated extractions with the very dilute acid, although not registered as the exchangeable form by widely used exchange methods. The usual exchange methods therefore fall far short of registering the amount of hydrogen replaced by the heavy additions of alkaline magnesium compounds in the Cumberland loam that may be taken as representative of the heavier types of well-leached residual soils of humid regions. Full recognition should be given to the importance of *time* as a factor in the extensive fixations.

If the replaceable-hydrogen determinations be taken as a measure of the readily exchangeable hydrogen, and the magnesium absorptions be taken as an actual measure of total replaceable hydrogen, it is evident that the Cumberland loam contains hydrogen ions that are held with different degrees of tenacity.

The incomplete recovery of the absorbed magnesium by the exchange reaction should not be taken to indicate that the solubility of the quantities absorbed from economic additions is so low as to prevent absorbed magnesium from entering readily into the free soil-water. On the contrary, the outgo of magnesium from such additions shows that the absorption complex is readily hydrolyzed—and more so than corresponding quantities of absorbed calcium.

The fact that the initial rapid disintegration of excessive additions of alkaline earth carbonates is followed by a subsequent slower decomposition during a long period of time had been determined at the Tennessee station (4) by another line of attack. For want of a better terminology, the more intensive initial reaction between soil and excesses of added carbonates was at that time designated as "Immediate Lime Requirement," whereas the extended reaction was designated as "Continuous Lime Requirement." The present experiments confirm the conclusion that there are present in the soil certain acid complexes that undergo rapid reaction with alkaline earths added in moderate or economic amounts, whereas there are other acid compounds that react only when excesses of carbonates are added and extended periods of contact are permitted. The two conditions, excessive additions and extended period of contact, were imposed in both the initial and present experiments.

It should be emphasized, however, that the speed of magnesium absorptions

from heavy additions of the more soluble alkaline magnesic carbonates was much greater than that found for chemically equivalent amounts of the less soluble carbonate of calcium. The mass-action effect of the more soluble magnesic materials apparently causes the heavy additions of magnesium to enter into the absorbed state to a much greater extent than that found for the less soluble calcium carbonate. The corollary fixation of calcium is under consideration for separate presentation.

A comparison of the recoveries registered by the several methods in the data of tables 2, 4, 5, and 6 is shown graphically in figure 1, the "increase" values of table 1 being taken as 100 per cent.

SUMMARY AND CONCLUSIONS

As a sequence to certain cylinder and lysimeter experiments relative to the specific absorptions found for seven calcic and magnesic materials, an adjunct lysimeter installation was used to determine the influence of form and amount of the "light" and "heavy" oxides and carbonates and the normal carbonate of magnesium upon the extent and nature of magnesium absorptions during a 4-year period.

The quantities of magnesium absorbed from 32-ton additions were much greater than those found for 8-ton treatments, but the minimal absorption greatly exceeded the exchange capacity registered by conventional methods.

The absorbed magnesium was found to be resistant to eight successive leachings, and also to four successive extractions, with a normal solution of ammonium chloride, the values obtained by the two procedures being comparable.

Since immediate additions equal to the unabsorbed residues were completely recovered by the first of eight ammonium chloride leachates, the prolonged recovery of the absorbed magnesium by multiple leachings was found to be attributable to a continued yield of magnesium from the absorption complex, and not to direct solvent action upon the unabsorbed magnesium residues.

The exchange capacities of the untreated soil and those of the magnesium-treated soils were found to be identical by the Kelly-Brown procedure.

Dilute acid extractions were found to be more efficacious than either leachings or extractions with ammonium chloride in effecting recoveries of absorbed magnesium.

Although none of the exchange methods registered quantities comparable to the amounts of magnesium actually absorbed, four overnight HNO_3 extractions of 0.02 maintained normality, with concomitant "acid neutralized" determinations, showed respective recoveries equal to those obtained by digestion with strong HCl.

A definite increase in the alumina dissolved from the magnesia-treated units indicated that the added magnesium had disrupted the aluminum complex.

Since both the lysimeter history and the laboratory determinations for each

soil unit showed that neither calcium nor potassium had been replaced by the added magnesium, the magnesium absorptions are accounted for only by hydrogen replacement; but the exchangeable hydrogen by the conventional methods was only one-tenth the equivalent of the maximal magnesium absorption. Hence, in relation to and confirming results from a different method of attack, it was concluded that in the soil system are two types of acid complexes. One of these reacts readily with economic quantities of magnesic materials to form exchangeable complexes, whereas the other type will react much more extensively with excessive incorporations over an extended period, to form absorption complexes not measurable by conventional methods, although measured by successive agitated extractions with 0.02 *N* nitric acid.

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CALCIUM CYANAMID AS A NITROGENOUS FERTILIZER[1]

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Calcium cyanamid, the first of the synthetic-nitrogen fertilizers, was introduced commercially in the early part of the twentieth century. That produced in America, and used in the experimental work reported in this paper, is grayish-black in color and contains 22 per cent nitrogen and calcium equivalent to 70 per cent hydrated lime. It is available in both pulverized and granular forms. The former is oiled to prevent undue dustiness. The latter is free of dust and consists of small pellets, passing a 12-mesh screen.

Considerable research has been conducted to determine whether calcium cyanamid will meet all the requirements of a nitrogenous fertilizer. The early literature dealing with its use is very inconsistent, excellent results having been obtained from its use in many instances, but unsatisfactory results or actual injury to the crop in others. More recent investigations show that when properly used, it gives satisfactory results.

When a new material having radically different characteristics is compared with a product the method of use of which has been standardized, the new material is often at a disadvantage. The present study was undertaken for the purpose of clarifying the situation with reference to calcium cyanamid. Care was taken in all of the experiments dealing with nitrogen availability to use the calcium cyanamid under conditions most favorable to its full efficiency.

The work here reported on calcium cyanamid was planned to give definite information on the following points:

The availability of its nitrogen (crop yields in comparison with other nitrogenous fertilizers).
The loss of nitrogen by leaching in comparison with other nitrogenous materials.
Its effect on the physical and chemical properties of the soil.
Its effect on the soil reaction.
Its use as a weed controlling agent.

Fertilizers used. The calcium cyanamid used in these investigations was the regular commercial calcium cyanamid produced by the American Cyanamid

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Company at Niagara Falls. Fresh samples were obtained at frequent intervals. This material has approximately the following composition: calcium cyanamid 63 per cent, free hydrated lime 17 per cent, graphitic carbon 12 per cent, limestone impurities 4 per cent, and oil 4 per cent. The oil is replaced by calcium nitrate in the granular calcium cyanamid.

In all of the regular nitrogen-availability studies, a generous supply of superphosphate and muriate of potash was added to the soil at the time the nitrogenous fertilizers were applied, thus eliminating the possibility of a deficiency of phosphoric acid or potash.

Methods of applying the fertilizers. When nitrogenous fertilizers were used as a top-dressing, they were applied as evenly as possible by hand, early in the spring, and while the vegetation was dry.

All other applications were made about 1 week before the seeds were planted. Each fertilizer was thoroughly mixed throughout the soil in the pot, or to a depth of about 4 inches in cylinder and plot experiments.

Preparation of samples and methods of analysis. Crops were usually harvested at or near maturity. Samples were then dried in the hot air or electric oven, and they were ground for analysis.

The total nitrogen was determined by the official Kjeldahl-Gunning-Arnold method. Duplicate determinations were run on each sample, and if they did not check within 0.1 per cent nitrogen, the analysis was repeated in duplicate. One-gram samples were used for analysis.

PRESENTATION OF RESULTS

Effect of continued use of various nitrogenous fertilizers on the crop yields

A Sassafras-loam soil with a pH of 5.8 was screened and well mixed. Sixteen pounds of this soil was then placed into each of five 2-gallon coffee-urn-shaped glazed pots.

Each pot was treated with 1 gm. of triple-superphosphate (41 per cent) and 1 gm. of muriate of potash for each crop grown. The nitrogenous treatments were made at the rate of 429 mgm. of nitrogen per pot for each crop. Eleven crops were grown in each pot. At the end of the experiment, each pot had received the equivalent of about 1,000 pounds of nitrogen per 2,000,000 pounds of soil.

Table 1 shows the crop yields and the amount of nitrogen contained in each. This table also shows the total crop yield, and the milligrams of nitrogen contained in each of the 11 crops. The experimental data indicate that the several carriers of nitrogen differ considerably in their effect on crop yields if the applications of each material are repeated a number of times on the same soil. The highest total yield was obtained by the use of animal tankage, followed closely by calcium cyanamid. The nitrogen recovery figures place calcium cyanamid first with 65.9 per cent recovery, sodium nitrate second, tankage third, and ammonium sulfate last with a nitrogen recovery of 36.4 per cent.

Sturkie and Bailey (23) reported similar effects with the continued use of calcium cyanamid, sodium nitrate, and ammonium sulphate upon crop yields. Their plots were treated annually with 22.5 pounds of nitrogen per acre over a period of 20 years or a total of 450 pounds of nitrogen was applied. Five different crops were grown on each plot during the last three years of the test. When the total of these five crop yields, for each plot, is taken, and the yield produced by calcium cyanamid taken as 100, then the sodium nitrate rating is 73, no nitrogen 49, and ammonium sulphate 25.

TABLE 1

Effect of various nitrogen fertilizers on nitrogen recoveries of 11 crops grown in succession on same soil*

SOIL TREATMENT	YIELDS IN DRY WEIGHTS												
	Corn	Corn	Corn	Corn	Corn	Wheat	Barley	Barley	Corn	Corn	Corn	Total 11 crops	
	gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	
No nitrogen	11.3	9.8	5.5	6.6	9.5	1.7	2.0	1.4	10.7	6.5	14.7	79.7	
Sodium nitrate	25.0	18.0	18.0	12.0	14.4	5.2	4.4	1.2	9.0	10.5	24.0	141.8	
Ammonium sulfate	34.0	18.0	14.0	11.6	23.2	4.6	0.9	0.2	3.0	3.2	3.0	115.5	
Calcium cyanamid	26.5	17.2	19.0	13.4	19.0	6.7	4.7	1.8	14.3	15.0	30.0	167.6	
Animal tankage	25.0	17.1	16.5	15.5	19.1	5.0	4.5	1.7	17.0	15.0	33.1	169.5	

Nitrogen contained in harvested crops

	mg.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*per cent recovery*
No nitrogen	217	102	80	104	123	43	48	52	175	97	128	1,169	
Sodium nitrate	535	398	473	368	403	274	201	59	355	378	319	3,763	55.0
Ammonium sulfate	544	364	380	376	549	213	18	9	155	136	142	2,886	36.4
Calcium cyanamid	504	344	486	413	503	294	217	93	549	467	408	4,278	65.9
Animal tankage	355	246	326	387	389	188	196	74	595	477	417	3,650	52.6

* Enough of each material to supply 1,000 pounds of elemental nitrogen per 2,000,000 pounds of soil was evenly divided among the 11 crops grown.

Comparison of calcium cyanamid and sodium nitrate on wheat on small plots on various soil types

The purpose of this experiment with wheat, conducted in square-yard plots (pl. 1, fig. 1) on five different soil types, was to compare yields and nitrogen recovery from the use of calcium cyanamid and sodium nitrate. Calcium carbonate was added to each soil to bring the pH between 6 and 7.

The data in table 2 show that the calcium cyanamid gave higher average crop yields than did an equivalent amount of sodium nitrate. It is quite probable that more of the fall application of nitrogen was retained by the soil in the case of the plots receiving the calcium cyanamid than in the case of those treated with nitrate.

TABLE 2

Comparison of calcium cyanamid and sodium nitrate on wheat in small plots on various soil types

Each test in duplicate

SOIL TREATMENT*	STRAW		GRAIN		STRAW AND GRAIN	
	Dry weight	Nitrogen content	Dry weight	Nitrogen content	Nitrogen	
					Total	Recovery
	gm.	*gm.*	*gm.*	*gm.*	*gm.*	*per cent*
Portsmouth Loam						
No nitrogen	469	1.71	213	3.99	5.70	....
Calcium cyanamid	514	2.24	236	5.03	7.27	31.1
Sodium nitrate	478	2.15	212	4.45	6.10	18.3
Penn Silt Loam						
No nitrogen	428	1.63	183	3.78	5.41	....
Calcium cyanamid	517	2.56	226	5.24	7.80	46.6
Sodium nitrate	507	2.28	198	4.70	6.98	30.9
Sassafras Loam						
No nitrogen	400	1.04	205	3.14	4.18	....
Calcium cyanamid	620	2.27	295	5.16	7.43	64.0
Sodium nitrate	615	2.15	262	4.58	6.73	50.2
Sassafras Silt Loam						
No nitrogen	177	0.58	80	1.26	1.84	....
Calcium cyanamid	432	1.59	166	2.92	4.51	50.4
Sodium nitrate	469	1.46	199	3.39	4.85	58.0
Sassafras Sand						
No nitrogen	182	0.59	92	1.47	2.06	....
Calcium cyanamid	344	1.03	172	3.08	4.11	40.3
Sodium nitrate	439	1.20	209	3.38	4.58	49.6
Average of all plots						
No nitrogen	331	1.11	161	2.73	3.84	....
Calcium cyanamid	485	1.93	218	4.28	6.21	46.5
Sodium nitrate	501	1.84	215	4.09	5.93	41.4

* Each plot received 640 pounds superphosphate and 320 pounds muriate of potash per acre in the fall. Nitrogen added at rate of 54.2 pounds per acre, one-third in fall a week before planting, and two-thirds as a top-dressing in late March. Each treatment was duplicated.

Comparison of effects of various nitrogen carriers on wheat grown in Latin-square field plots

A field was divided into 25 plots by the Latin-square method. Each plot measured 4 by 6 yards. A 2-foot buffer strip of soil separated each of the plots from its neighbor. Each nitrogen material was used on five plots which were arranged in such a way that no treatment ever appeared more than once in any row of five plots in either direction.

The nitrogenous fertilizers were applied at the rate of 55 pounds of nitrogen per acre. One-third of this amount was applied at the time of planting and the other two-thirds used as a top-dressing early in the spring.

The results shown in table 3 give evidence that there is little or no difference in the availability of the nitrogen of the various materials used. Urea gave a slightly lower recovery of nitrogen, but the difference is within the limits of experimental error.

TABLE 3

*Comparison of effects of various nitrogen carriers on wheat grown in Latin-square field plots**

SOIL TREATMENT†	STRAW		GRAIN		STRAW AND GRAIN	
	Dry weight	Nitrogen	Dry weight	Nitrogen	Dry weight	Nitrogen
	kgm.	*gm.*	*kgm.*	*gm.*	*kgm.*	*gm.*
Check	8.40	19.1	4.67	82.6	13.07	101.7
Calcium cyanamid	9.86	31.7	5.51	109.2	15.37	140.9
Urea	10.20	31.2	5.14	100.3	15.34	131.5
Ammonium sulfate	10.40	28.5	5.15	113.2	15.55	141.7
Sodium nitrate	10.26	30.8	5.34	109.4	15.60	140.2

* Average of five plots of each.

† Nitrogen applied at rate of 55 pounds of the element per acre.

Comparison of effect of various nitrogen carriers (in cylinders)

The cylinders used in these experiments are the type of those which have long been in use at the New Jersey station (10).

Series 1. The surface soil selected for this series of 20 cylinders was collected from a field on the college farm and was classified as Sassafras loam. A quantity of soil sufficient to supply each cylinder with 175 pounds on the air-dry basis was sifted and thoroughly mixed before being distributed in the cylinders.

Two crops per year, a late summer crop followed by rye or wheat, were harvested from each cylinder. The nitrogen fertilizers for the winter crops were applied each year, about the middle of October, in order to determine indirectly the relative amount of nitrogen lost by winter leaching from each source of fertilizer.

The tests indicate (table 4—winter crops) that if nitrogenous fertilizers

other than the nitrates are applied late in the fall to a heavy soil on which winter grain is planted, there may be only moderate losses of nitrogen by leach-

TABLE 4

Crop yields and nitrogen recovery in cylinders

Each figure represents average of two cylinders

SOIL TREATMENT *	SUMMER CROPS						WINTER CROPS				
	Corn	Buckwheat	Oats	Corn	Total yields	Nitrogen recovery	Wheat	Rye	Rye	Total yields	Nitrogen recovery
	gm.	gm.	gm.	gm.	gm.	per cent	gm.	gm.	gm.	gm.	per cent
Sassafras Loam											
	Dry weight						Dry weight				
No nitrogen	75	95	39	39	248	.....	77	35	57	169	.....
Sodium nitrate	124	149	68	128	469	.....	96	52	80	228	.....
Ammonium sulfate	131	146	72	119	468	.....	126	105	93	324	.....
Calcium cyanamid	141	141	84	122	488	.....	138	131	120	389	.....
	Nitrogen content						Nitrogen content				
No nitrogen	0.70	1.30	0.59	0.30	2.89	.....	0.53	0.42	0.32	1.27	.....
Sodium nitrate	1.50	2.59	1.47	1.01	6.57	71.88	0.63	0.39	0.44	1.46	4.95
Ammonium sulfate	1.33	2.63	1.38	0.91	6.25	65.62	0.89	0.91	0.55	2.35	28.13
Calcium cyanamid	1.52	2.34	1.57	0.89	6.32	66.99	0.94	1.00	0.63	2.57	33.84
Sassafras Sand											
	Dry weight						Dry weight				
No nitrogen	74	....	....	41	115	.....	55	33	54	142	.....
Sodium nitrate	71	....	....	143	214	.....	70	32	59	161	.....
Ammonium sulfate	68	....	....	138	206	.....	66	48	56	170	.....
Calcium cyanamid	83	....	....	132	215	.....	96	105	94	295	.....
	Nitrogen content						Nitrogen content				
No nitrogen	0.79	....	....	0.29	1.08	.....	0.37	0.22	0.37	0.96	.....
Sodium nitrate	1.14	....	....	1.00	2.14	41.40	0.45	0.22	0.37	1.04	2.08
Ammonium sulfate	1.09	....	....	1.07	2.16	42.19	0.43	0.33	0.34	1.10	3.65
Calcium cyanamid	1.18	....	....	0.80	1.98	35.16	0.68	0.76	0.59	2.03	27.86

* Each cylinder received the equivalent of 640 pounds superphosphate and 320 pounds muriate of potash per acre, at the time nitrogen fertilizers (supplying 41 pounds of nitrogen per acre) were applied.

ing. This is due to the fact that the ammonium ion is held firmly by the base-exchange complex of the soil, and must be converted to nitrite or nitrate before

it will be leached out to any extent. In this test, the nitrogen applied as sodium nitrate had little effect upon the crop growth, whereas ammonium sulfate and calcium cyanamid, especially the latter, gave a reasonably good increase in the crop growth and there was a fair percentage-recovery of the added nitrogen.

Street (21) working with lysimeters containing 20 inches of soil found that during a 12-month period, approximately 70 per cent of the nitrogen from sodium, calcium, and potassium nitrate was lost by drainage as compared to 60 per cent from ammonium sulfate, ammonium phosphate, and dried blood; 53 per cent from urea, castor pomace, and horn and hoof meal; 44 per cent from

TABLE 5

Crop yields and nitrogen recoveries from use of varying amounts of calcium cyanamid

SOIL TREATMENT	CORN*	BUCKWHEAT*	CORN†	CORN†	AVERAGE ALL CROPS	NITROGEN RECOVERY
	gm.	*gm.*	*gm.*	*gm.*	*gm.*	*per cent*
No nitrogen	77	56	62	60	63	
100 lbs. calcium cyanamid	138	82	123	95	109	
200 lbs. calcium cyanamid	208	100	156	131	148	
300 lbs. calcium cyanamid	247	115	202	168	184	
400 lbs. calcium cyanamid	303	120	238	205	216	
Yield of nitrogen (summer crops)						
No nitrogen	0.578	0.805	0.477	0.472	0.583	
100 lbs. calcium cyanamid	0.918	1.118	0.802	0.781	0.904	46.01
200 lbs. calcium cyanamid	1.431	1.713	1.043	1.062	1.312	52.72
300 lbs. calcium cyanamid	1.696	2.179	1.590	1.322	1.696	53.76
400 lbs. calcium cyanamid	2.181	2.462	2.046	1.969	2.164	57.34

* 1931. † 1932.

animal tankage, fish, linseed meal, and cottonseed meal; and 30 per cent from calcium cyanamid and cow manure.

Series 2. The surface soil selected for this series of cylinders was an acid Sassafras sand. One hundred grams of ground limestone was added in order to bring the pH to near neutrality. In all other respects series 1 and 2 were identical.

Data in table 4 (summer crops) show no great difference in the crop yields produced by the various fertilizers.

The winter crop yields (table 4) indicate that little of the calcium cyanamid nitrogen was lost, even from a sand, where the fertilizer was applied about the middle of October. The greater retention of the nitrogen of calcium cyanamid is no doubt due to the relatively slow nitrification which has been reported (6).

Series 3. A third series of cylinder tests was carried out in order to determine whether the nitrogen from large applications of calcium cyanamid was

used as efficiently by plants as that from small applications. During the fall, winter, and spring months, a crop of rye was grown in order to determine the relation between the rate of application and the amount of nitrogen recovered in the crop.

A Penn loam soil was selected for this test. The nitrogen treatment ranged from no nitrogen to the equivalent of 400 pounds of calcium cyanamid per acre.

The data given in table 5 indicate an increasing percentage recovery of the nitrogen as the rate of application increases from 100 to 400 pounds per acre.

When heavy applications of calcium cyanamid are made to soil, nitrification is retarded and may be almost entirely stopped for some time. In the case of fall applications no nitrates may be produced until the following spring. On the other hand, if the application is small and the calcium cyanamid is thoroughly mixed with the soil (table 6), the nitrification processes may be retarded very little and considerable nitrogen may be leached out. Accordingly, fall applications, if small, should not be made until after the soil temperature has

TABLE 6

*Crop yields and nitrogen recoveries from use of calcium cyanamid applied in different amounts**

Winter crops

AMOUNT APPLIED PER ACRE	DATE OF APPLICATION	DRY WEIGHT	NITROGEN	
			Content	Recovery
lbs.		*gm.*	*gm.*	*per cent*
0	.....	80	0.61	.....
200	October 8	116	0.91	21.45
300	October 8	125	1.20	28.34
400	October 8	166	1.65	37.45

* Crops planted October 15.

fallen to the point at which nitrification is relatively slow. Fall applications should not be delayed until the ground freezes, since under such conditions satisfactory results are not obtained. The reason for this is not entirely clear. No difficulty is experienced if the calcium cyanamid is applied in the fall before the soil freezes or if it is applied in the spring after the frost is largely out of the ground.

Cowie (5) has shown that the conversion of the nitrogen of calcium cyanamid to urea is not dependent upon microörganisms, but may be accelerated by various catalytic agents present in the soil. Most soils contain an abundance of urea organisms which convert urea to ammonia even under conditions far removed from the optimum as measured by nitrate formation. Therefore, there is little danger of the nitrogen being leached out as cyanamide or urea.

Comparison of various nitrogenous fertilizers in an acid sand

Mooers (13) has claimed that calcium cyanamid is not suitable for use in an acid sand. The difficulty is probably to be attributed to the low buffer ca-

pacity of the sand. Under such conditions dicyandiamid may be formed if the calcium cyanamid is not mixed thoroughly with the soil.

To make a test of this matter, 12 one-gallon, glazed earthenware pots were filled with an equal weight of an acid Sassafras sand. The nitrogenous treatments were made at the rate of 160 mgm. of nitrogen per pot. The results given in table 7 are the average of each treatment run in triplicate. According to the results of this test, sodium nitrate is slightly superior to calcium cyanamid in a very acid sand. This is to be expected since the nitrate ion is more readily assimilated in an acid medium, as explained in the discussion. On the other hand, calcium cyanamid produced a much greater yield than did the physiologically acid fertilizer, ammonium sulfate.

Comparison of calcium cyanamid and sodium nitrate in a sand deficient in potassium

The purpose of this experiment was to determine whether in comparisons of calcium cyanamid and sodium nitrate the latter, by reason of its content of

TABLE 7

Effect of various nitrogen fertilizers on barley in an acid sand

TREATMENT	SOIL AT END OF TEST	DRY WEIGHT	NITROGEN	
			Content	Recovery
	pH	*gm.*	*mgm.*	*per cent*
No nitrogen	5.2	1.5	23.7	....
Ammonium sulfate	4.6	1.5	54.0	18.9
Calcium cyanamid	5.5	5.7	139.9	66.5
Sodium nitrate	5.4	7.1	146.7	76.8

sodium, might have an advantage when there is a deficiency of available potassium in the soil.

The soil selected was a Sassafras sand which contained very little nutrient material. Two-gallon glazed pots were used. Two grams of superphosphate was applied to each pot before each planting of corn in order that phosphate might not be a limiting factor in the growth of the plants. Calcium cyanamid and sodium nitrate were applied at rates necessary to supply 320 mgm. of nitrogen per pot for each crop. In the cases where muriate of potash and sodium chloride were added, the rate was 1 gm. of each per pot.

It is evident from the data shown in table 8 that the sodium of the sodium nitrate was of considerable value under conditions of a deficiency of potassium. The sodium served only partially as a substitute for potassium, as is apparent from the better results obtained by the use of muriate of potash.

Hartwell and Damon (9) have shown that where there is an insufficiency of potassium, sodium is generally useful. This benefit is believed to be partly indirect, as by the replacement of potassium by sodium in the soil complex,

and partly in its direct effect on the plant. In other words, sodium apparently substitutes in part for potassium in the growth processes of the plant. It is conceivable that in some cases investigators who have reported a higher efficiency of the nitrogen in sodium nitrate have been misled in their interpretations on account of not having taken into consideration the sodium of the nitrate of soda.

Comparison of the availability of the nitrogen of sodium nitrate, calcium cyanamid, dicyandiamid, and mixtures of the last two

The purpose of the experiment was to determine whether dicyandiamid nitrogen would be available if considerable time was allowed for it to be converted to other nitrogenous compounds.

TABLE 8

Comparison of calcium cyanamid and sodium nitrate on corn in a potassium-deficient sand

NUMBER	SOIL TREATMENT*	SERIES	DRY WEIGHT OF CROPS		
			Crop 1	Crop 2	Crop 3
			gm.	*gm.*	*gm.*
1	Calcium cyanamid	a	9.1	13.5	5.2
	No potash	b	9.8	14.6	(Lost)
2	Sodium nitrate	a	14.2	22.0	6.8
	No potash	b	14.5	23.5	8.1
3	Calcium cyanamid	a	13.1	23.8	6.4
	Sodium chloride	b	11.0	21.7	6.2
4	Sodium nitrate	a	11.8	19.0	6.6
	Sodium chloride	b	13.2	22.0	5.1
5	Calcium cyanamid	a	22.6	37.0	20.0
	Muriate of potash	b	23.5	36.0	22.2
6	Sodium nitrate	a	21.5	41.2	20.1
	Muriate of potash	b	21.2	42.7	20.7

* Superphosphate applied in all cases.

The tests were conducted in glazed earthenware pots in the greenhouse. Corn was grown in a Sassafras loam soil and also in a Sassafras sand in order to determine whether the nitrogen of dicyandiamid is more available in a heavy than in a light soil. The pH of both soils was between 6 and 7, at the beginning of the experiment. The nitrogenous materials were added at the rate of 330 mgm. of nitrogen per pot. The mixtures are listed in table 9. Only one application of nitrogen was made at the beginning of the experiment, but 2 gm. of superphosphate and 1 gm. of muriate of potash were added before each of the four successive crops in order that the lack of available phosphoric acid and potash might not become a limiting factor.

The results of the experiment reported in table 9 show that dicyandiamid, when used in sand or in an ordinary loam soil, is a slowly available source of nitrogen. As suggested by Richardson (19) the slow availability makes di-

TABLE 9

Efficiency of nitrogen of calcium cyanamid and dicyandiamid when used on four successive crops of corn

SOIL TREATMENT*	LOAM SOIL					SAND SOIL				
	Crop number									
	1	2	3	4	Total	1	2	3	4	Total
Dry weight										
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
No nitrogen	5.0	4.3	5.2	8.2	22.7	6.9	4.9	4.9	10.7	27.4
Sodium nitrate	7.4	7.8	7.0	9.9	32.1	8.1	8.1	6.9	12.0	35.1
All cal. cyanamid† 0 Dicy.‡	8.0	7.0	6.4	9.6	31.0	7.8	5.8	6.6	12.1	32.3
¾ " " ¼ "	6.5	6.1	9.1	9.4	31.1	7.9	6.0	5.9	11.4	31.2
½ " " ½ "	6.9	5.3	10.1	9.4	31.7	7.6	6.1	6.0	11.8	31.5
¼ " " ¾ "	5.4	6.0	10.5	10.5	32.4	7.0	5.3	5.5	10.9	28.7
0 " " all "	5.1	4.0	12.6	10.0	31.7	6.3	5.0	5.6	11.3	28.2
Nitrogen content										
	mg.	mg.	mg.	mg.	mg.	mg.	mg.	mg.	mg.	mg.
No nitrogen	93	67	50	62	272	167	100	58	92	417
Sodium nitrate	250	137	69	74	530	270	192	79	95	636
All cal. cyanamid† 0 Dicy.‡	253	123	60	75	511	294	190	95	96	675
¾ " " ¼ "	191	162	96	74	523	279	134	73	94	580
½ " " ½ "	198	119	102	71	490	274	123	73	95	565
¼ " " ¾ "	165	155	135	77	532	264	110	66	89	529
0 " " all "	156	94	152	75	477	248	111	66	97	522
Nitrogen recovery										
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Sodium nitrate	47.5	21.2	5.7	3.7	78.1	31.5	27.9	6.3	0.8	66.5
All cal. cyanamid† 0 Dicy.‡	48.5	16.8	3.0	4.1	72.4	38.5	27.2	9.6	1.1	76.4
¾ " " ¼ "	29.6	28.7	13.9	3.7	75.9	34.2	10.4	4.5	0.4	49.5
½ " " ½ "	31.9	15.5	15.7	2.9	66.0	32.4	7.1	4.7	0.7	44.9
¼ " " ¾ "	21.8	26.7	25.8	4.4	78.7	29.4	3.2	2.5	−.9	34.2
0 " " all "	18.9	8.0	30.9	4.1	61.9	24.7	3.5	2.6	1.2	32.0

* Nitrogen materials added at the rate of 330 mgm. of nitrogen per 2-gallon pot.

† Calcium cyanamid.

‡ Dicyandiamid.

cyandiamid an unfavorable source of nitrogen for plants having a short growing season, but there may possibly be some advantages to its use in mixtures with other sources of nitrogen that are to be used for winter grain or grassland fer-

tilization. That most of the nitrogen in dicyandiamid is finally available in certain soils is proved by the data (table 9).

Doldi (7) claims that the nitrogen of dicyandiamid is as readily available as that in sodium nitrate in a soil containing 36 per cent organic matter, but that its availability decreases with a decrease in the organic matter of the soil in which it is used. Murata (14) found that ammonification of dicyandiamid was rapid under water-logged paddy-field conditions, and that it is an excellent source of nitrogen for rice.

Allison, Skinner, and Reid (2) found that dicyandiamid was actually injurious to some plants, but did not cause any definite injury other than tip

TABLE 10

Yields and content of nitrogen in crops from use of various forms of calcium cyanamid

TREATMENT NUMBER	CALCIUM CYANAMID	RAPE		BUCKWHEAT	
		Dry weight	Nitrogen content	Dry weight	Nitrogen content
		gm.	*mgm.*	*gm.*	*mgm.*
1	None	6.93	125.1	11.03	151.7
2	Pulverized	15.83	379.3	11.87	304.2
3	Granular (composite sample)	14.93	403.3	10.77	295.2
4	Granular through 20 on 30 mesh	16.07	368.3	11.63	310.5
5	Granular through 12 on 14 mesh	15.53	368.1	11.03	285.1
6	Granular through 10 on 12 mesh	14.37	363.7	10.80	287.5
7	Granular through 8 on 10 mesh	13.43	349.6	10.47	277.2
8	Granular* 90 per cent nitrogen ration	15.13	355.5	11.20	295.1
9	Granular* 90 per cent dicyandiamid 10 per cent	15.10	391.9	9.83	274.8
10	Granular* 95 per cent nitrogen ration	15.70	369.7	11.57	299.1
11	Granular* 95 per cent dicyandiamid 5 per cent	15.00	361.4	9.37	283.1
12	Granular* 97½ per cent nitrogen ration	15.40	361.8	11.30	289.5
13	Granular* 97½ per cent dicyandiamid 2½ per cent	15.13	371.2	11.23	315.4

* Through 10-mesh screen.

burning to corn. The results reported in this paper show almost as great recovery of nitrogen from dicyandiamid over a 5-month period, when used on a loam soil, as was obtained from sodium nitrate and calcium cyanamid. The recovery was not as great for the dicyandiamid in the case of the sand.

Comparison of availability of the nitrogen of pulverized and granular calcium cyanamid

The granular calcium cyanamid used in these experiments contained, in addition to cyanamide nitrogen, approximately 1.25 per cent of nitrate nitrogen. The percentages of particles (commercial granular calcium cyanamid) passing through the 12, 14, 20, 30, 40, 60, and 80-mesh screens were 99, 91, 60, 24, 11, 3, and 0.4 respectively.

This experiment was conducted in the greenhouse. The soil used was a Sassafras loam with a pH of 6.3. Rape and buckwheat were used as the test crops. Nitrogen was supplied to the extent of 330 mgm. per pot, except in the case of treatments 8, 10, and 12 (table 10) where only 90, 95, and 97½ per cent of the full ration was used, respectively.

Three of the treatments (9, 11, and 13) contained part of their nitrogen in the form of C. P. dicyandiamid. Interest in this material arises from the fact that if calcium cyanamid is applied to the soils in large granules, or in heaps, there is a tendency for part of the nitrogen to be changed to dicyandiamid rather than to urea, as the calcium cyanamid reacts with the moist soil.

The conversion of calcium cyanamid to urea is catalyzed by certain minerals in the soil. It is most rapid at a pH of 7 or lower. If the granules are large, or if the material is applied in piles and not mixed with the soil, a high alkalinity develops which favors dicyandiamid formation in the interior of the granule or group of particles, at points out of direct contact with the soil. The alkalinity is due largely to the calcium hydroxide liberated by the action of the moist soil on calcium cyanamid. It is increased by the formation of ammonia as the decomposition proceeds.

At the beginning of the experiment, each pot was weighed and the moisture content of the soil was brought up to the optimum. Each day thereafter six pots were weighed, the average loss of water was determined, and that quantity of water added to each pot. At the end of each week all the pots were weighed and any discrepancies in the moisture content were corrected.

The results of this experiment indicate that it is not advisable to have the calcium cyanamid granules too large. The use of the smaller sized separates of granular calcium cyanamid results in crop yields and nitrogen recoveries equal to those obtained from the pulverized calcium cyanamid. When the larger granules were employed crop yields and nitrogen recoveries were somewhat lower.

The plants receiving treatments, 6, 7, and 9, especially the last two, showed some tip-burning. This is characteristic of plants fertilized with dicyandiamid. This material is relatively stable in the soil, its nitrogen becoming available to the plant very slowly.

Comparative effect of nitrogen carriers on soil reaction

The primary purpose of this experiment was to determine the effect of various nitrogen carriers on the reaction of the soil:

In the presence of a crop, soil not leached.
In the presence of a crop, soil leached.
In the absence of a crop, soil not leached.
In the absence of a crop, soil leached.

The secondary purpose was to determine the effect of the fertilizer treatments on the crops grown.

A Sassafras loam soil was well mixed and screened. Sixteen-pound portions were then placed into each of 52 two-gallon glazed coffee urns. The holes in the bottom of 26 of the urns were closed with rubber stoppers. One-hole rubber stoppers, fitted with glass tubing which led to individual 2½-liter bottles, were placed in the openings of the other 26 urns.

Five crops of barley and five crops of corn were grown in each pot. Each pot received the equivalent of 50 pounds of K_2O, 60 pounds of P_2O_5 (with the exception of No. 11 which received extra phosphoric acid), and 50 pounds of nitrogen per acre (with the exception of No. 1), before each crop was planted. At the end of the experiment, 500 pounds of K_2O, 500 pounds of nitrogen, and 600 pounds of P_2O_5 (on the acre basis) had been added per pot. All the K_2O was applied as muriate of potash.

Seven and one-half liters of water were passed through each leached soil on which a crop was grown. Five liters were passed through each leached soil where no crop was grown.

The differences in the crop yields produced by the several fertilizer applications (table 11) are not important, being probably within the limits of experimental error.

When calcium cyanamid or nitrate of soda was used in conjunction with orthophosphoric acid or ammonium phosphate, the net effect was a marked rise in the pH of the soil. A somewhat smaller rise in pH occurred in the case of the calcium nitrate treatments. All other treatments resulted in a lowering of the pH. This was especially noticeable following the use of ammonium sulfate. The test indicates that it is possible to balance the acid effects of orthophosphoric acid and ammonium phosphate by the supplemental use of alkaline carriers of nitrogen such as calcium cyanamid, sodium nitrate, and nitrate of lime.

Very little difference was noted between the effects of sodium nitrate and calcium cyanamid on the pH of the soil, most likely because the Sassafras loam used in this experiment was fairly well buffered. Fudge (8) and Pierre (15), however, have found that calcium cyanamid causes a greater decrease in the acidity of the soil than does sodium nitrate. The results of the unsaturation test (table 11) tend to confirm their results.

Effect of various nitrogenous fertilizers and hydrated lime on the pH of the soil

A Sassafras loam soil with a pH of 5.4 was used to determine the effect of the various materials on the reaction of the soil. The tests were carried out in 1-gallon glazed earthenware pots.

Calcium cyanamid and C. P. hydrated lime were each applied at the rate of 1,000 pounds per acre. The other nitrogen materials were applied in such amounts as to add the same quantity of nitrogen as that supplied by calcium cyanamid. All materials were thoroughly mixed with the soil.

The soil moisture was kept as near the optimum for the particular soil as was possible. After 60 days, corn was seeded in each pot in order to remove excess

TABLE 11

Effect of various nitrogen fertilizers upon growth and nitrogen content of crop and pH of soil

NUMBER	SOIL TREATMENT	SOIL NOT LEACHED				SOIL LEACHED			
		Dry† weight	Nitrogen content	pH of soil		Dry† weight	Nitrogen content	pH of soil	
				Cropped	Not cropped			Cropped	Not cropped
		gm.	*mgm.*			*gm.*	*mgm.*		
1	No nitrogen. Phosphoric acid*	44.2	1,056	6.2	5.9	42.4	1,021	6.3	6.3
2	Calcium cyanamid plus phosphoric acid	69.6	2,761	6.9	6.1	63.2	2,477	6.9	6.5
3	Sodium nitrate plus phosphoric acid	65.9	2,827	7.0	6.1	58.3	2,127	6.8	6.4
4	Calcium nitrate plus phosphoric acid	68.6	2,730	6.6	6.0	57.5	2,047	6.5	6.3
5	Ammonium sulfate plus phosphoric acid	73.0	2,868	5.2	4.6	60.6	2,211	5.2	4.7
6	Nitric acid plus phosphoric acid	71.9	2,876	6.0	5.1	62.9	2,232	6.0	5.5
7	Ammonium hydroxide plus phosphoric acid	70.6	2,866	5.5	5.1	65.6	2,499	5.2	5.1
8	Ammonium hydroxide plus phosphoric acid and gypsum	70.1	2,923	5.4	5.1	63.1	2,429	5.3	5.1
9	Ammonium hydroxide plus superphosphate	68.4	2,811	5.9	5.3	66.2	2,503	6.0	5.2
10	Ammonium sulfate plus superphosphate	69.9	2,726	5.2	4.7	59.3	2,140	5.1	4.8
11	Ammonium phosphate (commercial 11–48–0)	71.1	2,815	5.4	5.1	61.6	2,211	5.4	5.2
12	Ammonium phosphate plus sodium nitrate	68.0	2,822	6.8	5.7	61.3	2,219	6.6	6.3
13	Ammonium phosphate plus ammonium sulfate	68.4	2,777	5.2	4.7	60.6	2,145	5.2	4.7

* Orthophosphoric acid.

† Total for 10 successive crops.

nitrate from the soil. Table 12 shows the materials used, the length of time after treatment at which pH determinations were made, and the pH of the soil of each pot.

Commercial calcium cyanamid contains calcium equivalent to about 70 per cent calcium hydroxide. Most of this calcium is in readily soluble and active forms [$CaCN_2$ and $Ca(OH)_2$]. When the $CaCN_2$ comes in contact with moist soil, it is rapidly broken down into urea and calcium hydroxide. The urea is rapidly converted to ammonia, which in turn is slowly converted to nitrate. While the nitrogen is in the form of ammonia, it aids the hydrated lime in raising the pH of the soil.

The net result of these various changes upon the pH of the soil is clearly shown in table 12. Calcium cyanamid caused the pH to rise considerably above that

TABLE 12

Effect of various nitrogen materials and of hydrated lime on the pH of Sassafras loam soil

Original pH 5.4

TREATMENT	pH AT FOLLOWING PERIODS AFTER TREATMENT								
	4 hours	1 day	4 days	7 days	11 days	16 days	32 days	60 days	After cropping corn
	pH	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
Calcium cyanamid*	6.5	6.6	6.8	6.6	6.6	6.5	5.7	5.3	5.7
Ammonium sulfate	5.4	5.3	5.1	5.0	5.0	5.0	4.5	4.4	4.9
Urea	5.6	6.1	6.1	5.9	5.3	5.2	4.6	4.6	5.1
Hydrated lime*	6.5	6.4	6.4	6.4	6.3	6.3	6.3	6.3	6.3
Urea and hydrated lime*	6.6	6.9	6.8	6.3	5.9	5.6	5.5	5.5	5.9
Ammonium sulfate and lime*	6.5	6.4	6.1	5.9	5.6	5.2	4.9	4.8	5.5

* 1,000 pounds per acre. Nitrogen materials applied in such amounts to give equal quantities of the element.

produced by an equal weight of hydrated lime, and then it slowly dropped to a value slightly below that of the soil before treatment. When a crop had been grown on the soil, the pH again rose somewhat above that of the original soil. In other words, the net effect of the calcium cyanamid on cropped soil was to raise its pH. Ammonium sulfate and urea, particularly the former, lowered the pH.

Effects of continuous use of various nitrogen materials on physical and chemical properties of the soil

After the eleventh crop was harvested from the pots used in the experiment on the effect of the continued use of the various nitrogenous fertilizers on the crop yield (table 1), the soil from each pot was thoroughly mixed and passed through a 2-mm. sieve, after which it was used for the following studies:

A portion of soil from each pot was used for a percolation experiment. Five

percolation tubes, 2 inches in diameter and deep enough to allow the addition of 12 inches of soil were set up. The same weight of each of the five soils was placed in the tubes. The water was applied in each tube. When the water began to percolate through the bottom of the tubes it was turned off, and the tubes were allowed to stand for 1 day. A constant flow of water was then sent through the top of each of the tubes, and the amount of water percolating through the soil in 16 hours was measured. The results are shown in table 13.

A second portion of each soil was taken to test the rate of settling of the soil colloids. Twenty-five gram portions of each of the soils were placed into calibrated graduates. To each graduate was added 100 cc. of distilled water. Each mixture of soil and water was then shaken for 2 minutes, and allowed to stand for 20 minutes. The photograph (pl. 1, fig. 2 a) was then taken of the five soils. Another photograph (pl. 1, fig. 2 b) was taken after 3 days' standing.

Another portion of each of the aforementioned soils was taken for pH determinations. The active acidity of each soil was determined by the potentio-

TABLE 13

Effect of nitrogen carriers on rate of percolation of water through soil

SOIL TREATMENT	PERCOLATE
	cc.
No nitrogen	405
Sodium nitrate	48
Ammonium sulfate	1,286
Calcium cyanamid	510
Tankage	1,248

metric method. The exchange acidity was determined by the use of indicators in a mixture of 1 part of soil and 2 parts of *N* Na_2SO_4.

A fourth portion of each of the five soils was analyzed for its base-exchange capacity and the percentage unsaturation at pH 7. Twenty grams of each soil was leached with neutral barium acetate until the pH of the leachate became neutral. The soil was then treated with a small amount of barium chloride solution and washed with water until the leachate gave no test for chlorine. This was done to insure the removal of all free barium not held by the base exchange complex.

The leachate from the barium acetate treatment was titrated against 0.1 *N* sodium hydroxide, and the milliequivalents of hydrogen per 100 gm. of soil calculated.

The total base-exchange capacity at pH 7 was then obtained by removing the barium from the soil by treatment with 0.1 *N* ammonium chloride which was continued until small portions of the leachate gave no precipitate when sulfuric acid was added. The number of milliequivalents of barium was then calculated for 100 gm. of soil by precipitating the barium as the sulfate. The per cent unsaturation was calculated (table 14).

The results of these experiments show that the several nitrogen materials employed in these tests are markedly different in their effects on the physical and chemical properties of the soil.

In the percolation and rate-of-settling studies, ammonium sulfate and tankage were outstanding in their effects. Water percolated through the soil treated with calcium cyanamid more rapidly than through the untreated soil. Their action was in marked contrast to that of sodium nitrate. The soil treated with sodium nitrate became very hard after wetting and being allowed to dry out. This undesirable physical condition caused the crop yields to fall as compared with those produced by calcium cyanamid and tankage.

In the base-exchange and pH studies, the definitely acid effect of the ammonium sulfate was quite apparent, as compared to the alkaline effects of sodium nitrate and calcium cyanamid. The soil treated with ammonium sulfate had dropped to pH 4.2, by the quinhydrone-electrode method, and

TABLE 14

Effect of nitrogen carriers on base exchange capaciiy and pH of soil

SOIL TREATMENT	HYDROGEN	BASE EXCHANGE CAPACITY	UNSATURATION	pH	
				Quinhydrone electrode	Colorimetric†
	*m.e.**	*m.e.**	*per cent*		
No nitrogen	3.62	11.40	34.8	5.9	5.6
Sodium nitrate	1.37	11.03	12.5	6.8	6.1
Ammonium sulfate	8.50	8.94	95.0	4.2	4.3
Calcium cyanamid	1.22	10.95	11.2	6.8	6.4
Tankage	4.12	11.03	37.5	5.8	5.4

* Per 100 gm. soil.

† In N Na_2SO_4.

had reached the stage of 95 per cent unsaturation at the end of the test. The yields had begun to fall by the end of the fifth successive crop.

Effect of the pH of the soil on the availability of the nitrogen of calcium cyanamid

An attempt was made in this experiment to determine the approximate pH at which the greatest recovery of nitrogen from calcium cyanamid takes place.

Three soils with a very low pH were selected for the test. The crops were grown in 2-gallon glazed earthenware pots. Each pot received 320 mgm. nitrogen in the form of calcium cyanamid. The pH of the soil was raised by adding increasingly larger amounts of calcium carbonate. Each treatment was run in triplicate, but, in order to conserve space, only the averages of the three pots are given in table 15. The pH readings were made after the crops were harvested.

The results of this experiment show that the nitrogen of calcium cyanamid is not used efficiently when the pH of the soil is very low. The barley crop,

which is sensitive to acid soils, gave very little growth at pH values below 5.0. It would appear from the results in table 15 that a pH of about 6.0 would have to be reached before a maximum recovery of nitrogen could be expected.

TABLE 15

Effect of varying the pH on recovery of nitrogen from calcium cyanamid

pH of soil	BARLEY			CORN		
	Dry weight	Nitrogen content		Dry weight	Nitrogen content	
	gm.	*per cent*	*mgm.*	*gm.*	*per cent*	*mgm.*
			On Sassafras sand			
4.9	1.57	1.59	25	4.73	1.61	76
5.5	10.37	2.25	233	13.63	1.91	261
6.4	12.67	2.08	263	15.75	2.00	311
6.8	13.83	2.08	287	17.87	1.87	335
7.1	12.27	2.17	266	16.70	1.91	319
7.3	11.35	2.23	253	15.60	2.07	323
7.5	11.45	2.28	261	13.67	1.87	265
7.6	12.00	2.28	273	12.65	2.02	256
			On Sassafras loam			
5.0	6.00	3.17	190	11.00	2.74	301
5.1	10.60	3.71	393	11.50	3.18	366
5.6	14.93	3.55	530	10.93	3.28	358
6.0	15.23	3.73	568	11.47	2.82	323
6.6	16.23	3.97	645	8.25	3.03	250
7.0	15.63	4.18	654	9.60	2.89	277
7.3	15.63	4.41	690	8.07	3.30	266
7.4	15.70	4.28	672	8.17	3.30	270
			On Penn silt loam			
4.6	0.70	1.14	8	4.25	1.60	68
4.7	1.20	1.67	20	7.57	2.26	171
5.1	3.43	3.09	106	10.37	2.61	271
5.4	7.77	2.60	202	11.80	2.70	319
5.7	8.60	2.81	242	9.87	2.59	256
6.1	8.93	3.16	282	8.77	2.85	250
6.3	9.33	2.93	274	10.23	2.73	279
6.7	10.60	3.00	318	9.83	2.98	293

Even at a pH considerably above the neutral point, for example 7.62, the crop growth was very near the maximum.

The corn crop is rather tolerant to soil acidity, and yet the results show that where the pH of the soil is below 5.0, the crop yields and the total nitrogen contained in the crops are low. At all pH values above 5.0 the corn plants made a good growth.

Calcium cyanamid as an agent for weed control in timothy

Two plots of timothy, each one-twentieth of an acre, were treated with the equivalent of 200 pounds of calcium cyanamid per acre. At the end of the growing season, the entire growth was weighed, and a representative sample of hay was taken from each plot. The different types of weeds were separated from the timothy and clover. Each separate was weighed and calculated on the acre basis.

The calcium cyanamid was applied early in the spring or just after the timothy and weeds had begun to grow. It was applied by hand early in the

TABLE 16

Effect of calcium cyanamid as a control for weeds in timothy (acre basis)*

	SEASON OF 1931				SEASON OF 1932			
	Total plants	Dry weight	Nitrogen	Protein	Total plants	Dry weight	Nitrogen	Protein
	per cent	*lbs.*	*per cent*	*lbs.*	*per cent*	*lbs.*	*per cent*	*lbs.*
Treated with calcium cyanamid								
Timothy	70.84	3,220	0.75	108.8	87.02	1,522	1.03	98.0
Clover	.....	.....	....	.....	0.34	6	2.04	0.8
Daisy	25.65	840	0.62	30.6	11.04	193	0.97	11.7
Miscellaneous weeds	3.51	115	1.42	10.2	1.60	28	1.21	2.1
Total	100.00	4,175	....	149.6	100.00	1,649	....	112.6
Not treated with calcium cyanamid								
Timothy	34.55	880	0.74	40.7	76.05	508	1.08	34.3
Clover	1.93	49	1.99	6.1	1.79	12	2.07	1.6
Daisy	59.67	1,520	0.41	39.0	11.83	79	0.64	3.2
Miscellaneous weeds	3.85	97	1.02	6.2	10.33	69	0.86	3.7
Total	100.00	2,546	....	92.0	100.00	668	....	42.8

* 200 pounds calcium cyanamid per acre.

morning while the dew was still on the plants, in order that more of the material might stick to the leaves.

These treatments would no doubt have been more effective if the calcium cyanamid had been applied with a dusting machine, which would have distributed it more evenly than is possible by a hand application.

The results of the treatments in 1931 and 1932 (table 16) both show an approximately 50 per cent control of the weeds. In each case, the yield of timothy was about three times as heavy on the treated plot as that produced on the check plot.

Bissy and Butler (3) were able to kill 80 per cent of the mustard in a grain field by applying 80 pounds of calcium cyanamid to the moist foliage. Sturkie

(22) was able to kill all the weeds on Bermuda-grass lawns with an application of 800 pounds per acre. Lighter applications were partially effective. Two thousand pounds per acre tended to injure or kill the leaves of the grass, but after a period of 2 weeks new leaves formed, and an excellent lawn was obtained.

DISCUSSION

Although the earlier investigations, prior to 1925, indicated that calcium cyanamid is not as available a source of nitrogen as are the common inorganic fertilizers, so considerable advancement has since been made in the knowledge of the correct methods of application that, with few exceptions, the more recent investigations have made it apparent that calcium cyanamid and the common inorganic nitrogenous fertilizers are of very nearly equal value as sources of nitrogen (11).

In an intensive investigation upon the decomposition of calcium cyanamid in the soil and its effects on germination, Crowther and Richardson (6) found that when calcium cyanamid is thoroughly mixed with the soil it is chemically converted to urea, which in turn is converted microbiologically to ammonia all within a few days. They concluded that its injurious effect on germinating seeds is caused by free cyanamid, which has a very high penetrating power and, therefore, the fertilizer should be applied some time before planting.

Buchanan and Barsky (4) made a study of the decomposition of calcium cyanamid in solution and point out that in soils of a pH below 7, dicyandiamid can not be formed from calcium cyanamid unless the latter is applied in such a manner that its alkalinity exceeds the buffering capacity of the soil.

Methods of use. Because of its peculiar properties, more care must be exercised in the use of calcium cyanamid than is necessary with most other nitrogenous fertilizers. The destruction of germinating seeds, which is so often mentioned, is caused by cyanamide itself, and not by its decomposition products (6). With proper methods of use, such as mixing the fertilizer with moist soil and allowing an interval of 3 days for every 100 pounds per acre between application of the fertilizer and planting of the crop this difficulty is overcome. Crowther and Richardson (6) also state that the decomposition of calcium cyanamid to urea can be accelerated by a number of minerals that may occur in the soil. Very few soils are deficient in the required catalyst, and the conversion of calcium cyanamid to ammonia is complete within a few days.

The "3 days for every 100 pounds" period is in most cases longer than necessary to overcome this effect of calcium cyanamid. In many of the preliminary tests on disease control (not all reported in this paper), the seeds were planted as soon as the fertilizer had been applied, and in no case did a 400-pound per acre application (mixed to a 6-inch depth) cause any retardation or decrease in germination. The foregoing recommendation should, however, be followed in order to be safe under conditions which are not favorable for the most rapid conversion—such as its use in a very sandy soil, or in soils with a low moisture content.

Calcium cyanamid is an alkaline material, having the property of being partially converted to dicyandiamid when it comes into contact with moisture unless an appropriate buffer, such as soil, is present to prevent the pH from rising above about 8.0. Commercial calcium cyanamid is stored and shipped in paper-lined bags in order to prevent it from coming in contact with moisture in the absence of soil. Bags should not be opened before the material is to be used, if the maximum efficiency of its nitrogen is desired.

As shown by Richardson (19), the same conversion also tends to take place when calcium cyanamid is mixed with superphosphate in such amounts as to exceed the acid content of the superphosphate.

Calcium cyanamid should not be applied in thick streams or piles, nor should it be applied as a side-dressing for vegetable crops unless it is mixed with the soil by cultivation soon after it is applied. Very heavy applications should be avoided on poorly buffered or alkaline soils. If these precautions are not taken, the alkalinity produced by the calcium cyanamid may greatly exceed the buffer capacity of the soil and some dicyandiamid, which is slowly available, may be formed. Good results are obtained by the use of calcium cyanamid as a top-dressing for pastures, but here again it should be allowed to fall on a board as it comes out of the drill, so as to spread it evenly instead of in seams. Top-dressings should be made early in the spring after the frost is out of the ground or in the fall before the ground freezes.

Calcium cyanamid should not be applied as a surface application to dry soil or to frozen soil. The soil should be moist and unfrozen so that the calcium cyanamid can diffuse into it and be subjected to action of the soil. Otherwise the calcium cyanamid, by lying on top of the dry soil and not diffusing into it, may be partly changed to dicyandiamid with consequent reduction in the availability of its nitrogen. Applications to dry surface soil should be made only if rain is imminent or if irrigation is to be practiced. In side-dressing cultivated crops, calcium cyanamid should be applied in the bottom of a newly-made furrow and mixed with the moist soil.

Nitrogen availability. The fact that all forms of nitrogen are not equally available for plant growth under all conditions has long been established. Because of numerous variable factors such as the reaction, type, temperature, and moisture content of the soil; the type of crop being grown; and the methods of distribution and time of application of nitrogen fertilizers, it is impossible to give any nitrogen material a definite rank as being more or less useful than another nitrogen material under all conditions.

The value placed on nitrates as sources of nitrogen has frequently been higher than that for calcium cyanamid, on the assumption that plants are more able to assimilate nitrogen in the nitrate form and that the nitrification of the nitrogen of calcium cyanamid is too slow. That this assumption is at least partially false has been proved by a number of investigations on the assimilation of the various forms of nitrogen by various plants. Tiedjens and Robbins (25) study-

ing the use of nitrate and ammonia nitrogen by certain crop plants, mainly tomatoes, soybeans, and peach seedlings, make the following statement:

> Theoretically, ammonia would seem to be a more efficient source of nitrogen than nitrates, as eventually ammonia is formed from nitrates in the process of synthesis of organic nitrogen. Likewise, in actual fact, ammonia in a nutrient solution at high pH proved to be a more quickly available form of nitrogen than nitrate, as indicated by more rapid stem elongation, greater leaf area, greater succulence, darker green color, and lower carbohydrate content of the plant tissue.

Prianishnikow (17) is of the opinion that nitrification is not a desirable process from the standpoint of plant nutrition, since less energy is expended in converting ammonia into protein than in converting nitrates. He also states that ammonia enters the plant faster than nitrates, and is more easily assimilated in the synthetic process. He claims that with an excess of ammonia, injury appears more readily than with an excess of nitrates, and that nitrification is, so to speak, a hygienic function which regulates the concentration of ammonia in the soil. According to his investigations (18), ammonium gives the better results in a neutral medium while in an acid reaction, nitrate is the better source of nitrogen for plants. By adjusting the hydrogen-ion concentration as well as that of the other cations present in the nutritive medium, the nutrition of the plant can be so altered that its optimum development will result from either the use of ammonia or of nitrate.

It has been claimed (1) that calcium cyanamid is a slowly-available source of nitrogen and that it is not satisfactory for use on crops which require most of their nitrogen during the earlier stages of their growth.

The retardation reported in the growth of cotton following the use of calcium cyanamid was probably due to the high concentration of ammonia. The common method of applying fertilizer to cotton has been to drill it into the old finishing furrow.[3] A center furrow is run through the fertilizer to spread it out somewhat and mix it with the soil. The soil is then bedded back and seeded. The rate of application, which did not compare favorably with other sources, was 80 pounds of nitrogen in row treatments. By the use of this method, the fertilizer would be very concentrated, causing a very slow nitrification. It is conceivable that the ammonia, which is held firmly in place by the base-exchange complex of the soil, was so concentrated in the portion of the soil which contains the roots of the cotton plant that ammonia injury resulted. Since plants, especially those low in carbohydrates, are not as sensitive to nitrate nitrogen, and since nitrate nitrogen is free to move in the soil, the same retardation would probably not result from the use of a nitrate or of any form of nitrogen which is rapidly converted to nitrate. Tiedjens (24) has demonstrated that ammonia is an excellent source of nitrogen for cotton when the pH is high, but in cultures where the pH was held near 3.5 and 4.5, the ammonia produced a very scant growth.

[3] Furrow left between rows at last cultivation of previous crop.

The investigations of Pirschle (16) show that ammonia is effective in producing abundant crop growth when the pH of the medium is near or above neutral (above pH 6.), but that nitrate nitrogen is the better source of nitrogen under acid conditions. In this respect calcium cyanamid has the unique property of raising the pH of the soil (table 12) higher than an equal weight of hydrated lime. As nitrification nears completion the pH is again lowered to near the value of the original soil. During the time that the nitrogen is in the form of ammonia, however, this property tends to hold the pH where it is more favorable for ammonia assimilation.

The relatively slow nitrification of calcium cyanamid is of value because ammonia nitrogen is not readily leached from the soil. This should be of considerable importance on the sandier types of soil, where fall-fertilization is practiced. The common practice of side-dressing is not as necessary where the nitrogen remains in the form of ammonia for a considerable period.

Effect upon the soil. The larger percentage of calcium contained in calcium cyanamid causes a flocculation of the soil colloids, and has a tendency to improve the physical condition of soils high in clay. In addition, calcium cyanamid has a greater tendency to counteract soil acidity and to increase the degree of saturation with bases than have any of the common nitrogenous fertilizers (20).

Dicyandiamid and the availability of its nitrogen. The literature contains many references to dicyandiamid. In some cases in which calcium cyanamid produced lower yields than did other nitrogenous fertilizers with which it was compared, dicyandiamid was mentioned as a probable cause of the lower yield. Although small amounts of dicyandiamid, when mixed and applied with other nitrogenous fertilizers, do not affect the nitrogen recovery to any appreciable extent, as shown in table 10 and reported by McGuinn (12) and others, there can be little doubt that improper methods of applying calcium cyanamid may result in the production of enough dicyandiamid in the soil to reduce the effectiveness of the nitrogen, since the nitrogen of dicyandiamid becomes available to plants only very slowly. However, if calcium cyanamid is well distributed over or mixed with moist soil, little or no dicyandiamid will be formed.

Dicyandiamid is not a particularly toxic form of nitrogen (6) but, because of its stability under ordinary soil conditions, its effects continue over a longer period. Under some conditions, such as in paddy-field fertilization, dicyandiamid is a valuable source of nitrogen.

Weed control. Pulverized calcium cyanamid is effective in destroying weeds which have a broad leaf. If it is applied when the weeds are young and when they are moist (after a rain or heavy dew), the dust adheres to the broad hairy leaves and as they dry they are killed. For this reason, it should never be used for killing weeds in vegetable plots (with the exception of asparagus) or other broad-leaved domestic plants, as the same principle applies. On the other hand, the leaves of grass plants are narrow and usually smooth on the upper surface so that less of the calcium cyanamid will adhere. There is usually some

injury to the exposed grass or grain leaves, causing a temporary change in the color of the foliage. In very extreme cases (21), the exposed part of the leaves may even be killed, but since the leaves grow out of a protected sheath the injury is only temporary and the unexposed portion soon replaces that which was injured.

Even distribution is of major importance in the destruction of weeds.

SUMMARY AND CONCLUSIONS

From the results of these experiments and the discussion, a number of conclusions may be drawn:

Calcium cyanamid, properly applied, gives crop yields equal to those produced by an equal amount of nitrogen from other high-grade materials. The nitrogen recovery is on the average equal for calcium cyanamid, sodium nitrate, ammonium sulfate, and urea.

In a very acid sand (under conditions that do not allow leaching—as in pots), sodium nitrate is slightly superior to calcium cyanamid, which in turn gives a much greater yield of dry matter and recovery of nitrogen than does ammonium sulfate.

The nitrogen from calcium cyanamid does not leach from the soil as readily as does that from inorganic nitrogenous materials.

The high percentage of calcium in calcium cyanamid has a beneficial effect upon the physical properties of the soil.

Calcium cyanamid causes a greater temporary decrease in hydrogen-ion concentration than does an equal weight of C. P. calcium hydroxide. It has a permanent physiologically alkaline effect.

Pulverized calcium cyanamid may be used to destroy weeds in grassland or small grains. It should be applied in the early spring and in the morning while the dew is still on the plants. The grass or grain itself usually changes from a green to a brownish color for a very short period, after which growth is rapid as a result of the available nitrogen present and of the elimination of a large percentage of the weeds.

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PLATE 1

FIG. 1. Sixty frames constructed from 2 inch by 12 inch boards, each frame 1 square yard in area. The frames have no bottoms and the added soil, previously screened and mixed, rests directly on the native subsoil.

FIG. 2. Settling of soil colloids. *A*. Twenty minutes after mixing. *B*. Three days after mixing. *1*, No nitrogen; *2*, calcium cyanamid; *3*, tankage; *4*, sodium nitrate; *5*, ammonium sulfate.

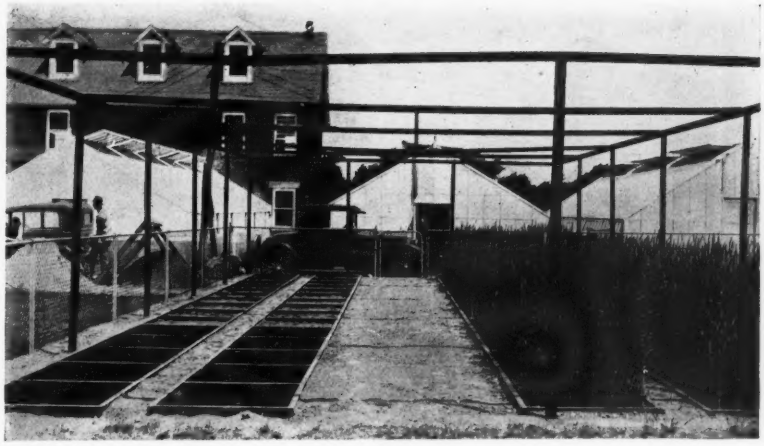
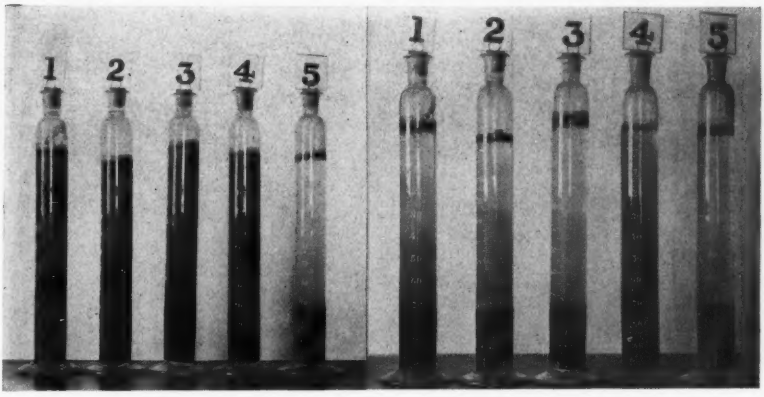


FIG. 1



A B

FIG. 2